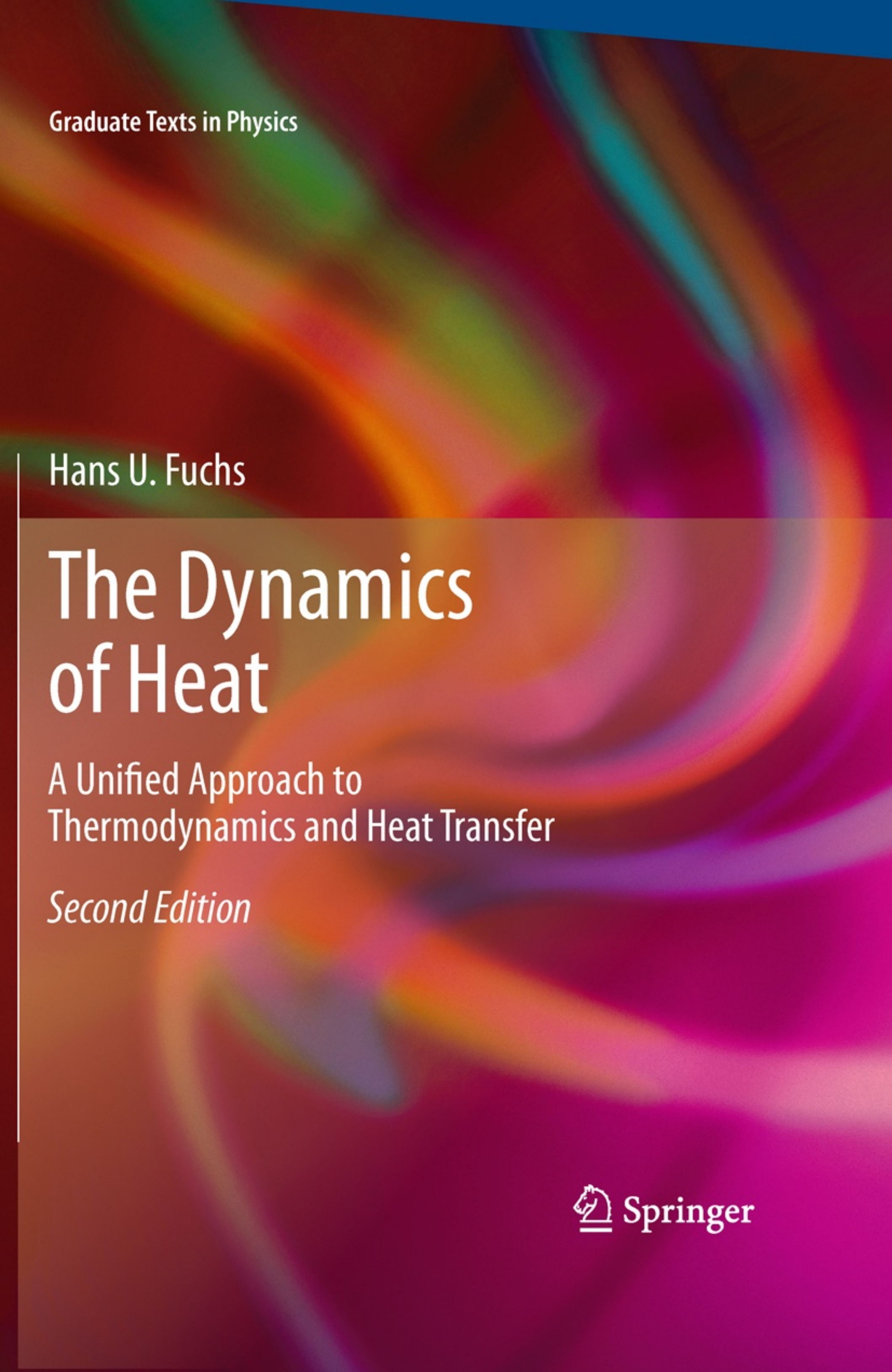

Graduate Texts in Physics

Hans U. Fuchs

The Dynamics of Heat

A Unified Approach to Thermodynamics and Heat Transfer

Second Edition

Springer

The Dynamics of Heat

GRADUATE TEXTS IN PHYSICS

Graduate Texts in Physics publishes core learning/teaching material for graduate- and advanced-level undergraduate courses on topics of current and emerging fields within physics, both pure and applied. These textbooks serve students at the MS- or PhD-level and their instructors as comprehensive sources of principles, definitions, derivations, experiments and applications (as relevant) for their mastery and teaching, respectively. International in scope and relevance, the textbooks correspond to course syllabi sufficiently to serve as required reading. Their didactic style, comprehensiveness and coverage of fundamental material also make them suitable as introductions or references for scientists entering, or requiring timely knowledge of, a research field.

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The Dynamics of Heat

A Unified Approach to Thermodynamics and Heat Transfer

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Preface to the Second Edition

The publication of this *Second Edition* of *The Dynamics of Heat* has given me the opportunity to make some major and, I hope, useful changes to the book. The character of the conceptualization of thermal processes—the direct approach to entropy as what in lay terms would be called "heat" and temperature as the corresponding potential—has been retained and much has been taken directly from the *First Edition*, but I have completely changed the structure of this text and I have added new material on thermal processes, chemical dynamics, and explicit dynamical modeling. The original goals of a unification of foundations and applications in general, and of thermodynamics and heat transfer in particular, have been the guiding principles for this revision. As such, *The Dynamics of Heat* continues to be a text that can help students of the applied sciences, engineering, and medicine to take the steps from the simplest beginnings in thermal and chemical physics all the way to more demanding and formal treatments of modern continuum thermodynamics. Students of physics can find an introduction to the foundations of a dynamical theory of macroscopic thermal phenomena that will complement modern treatments of statistical physics.

The book is now divided into four parts. Part I, *Processes, Energy, and Dynamical Models*, is an extensive revision of the Introduction of the *First Edition*. I have simplified the original brief description of the material and I have added explicit system dynamics modeling of laboratory experiments. Part II, *Thermal and Chemical Processes*, takes the introductory elements of the four main chapters of the previous edition and transforms them into an introduction to the dynamics of heat and substances suitable to a first college course on the subject. It builds upon the description of fluid, electrical, and mechanical phenomena introduced in Part I and essentially provides a uniform dynamical systems approach to models of thermal and chemical processes. Part IV, *Special Processes and Systems*, is the least changed from the previous text and contains the more advanced applications of the four large chapters of the *First Edition*. The Epilogue of the *First Edition* has been converted into Part III, *A Dynamical Theory of Heat*. which now offers a formal conclusion to Part II and an introduction to continuum thermodynamics and radiative transfer useful for the applications in Part IV. The Interlude of the First Edition which had the character of a historical and formal introduction to the thermodynamics of spatially uniform systems, has been omitted. For a direct approach to the dynamics of heat I now prefer the formalism of uniform processes developed in Part III over the classical treatment of cycles. Parts III and IV can be the foundation of an advanced course. Last but not least, the new *Introduction* is a brief outline of cognitive and historical aspects of human conceptualizations of nature in general and of thermal phenomena in particular.

A number of aspects of the text have been changed and some elements have been added. Here is a list of the most important of these changes and additions:

- There are descriptions including actual laboratory data for thermal and chemical phenomena in some key chapters. Many of the phenomena have subsequently been modeled with the help of simple system dynamics tools, providing explicit and detailed dynamical models. Additional experiments and models can be found on a Website for inquiry based learning (see below).

- Time dependent thermal and, especially, chemical phenomena have been given more space than in the previous edition. They can be found in Part II.
- A discussion of thermoelectricity has been added both in the introduction to thermal processes (Chapter 4) and in a more in-depth study of conductive processes (Chapter 13). This is another demonstration of the ease with which some subjects can be treated that are usually considered advanced material in standard texts.
- To strengthen the didactic approach to introductory continuum physics, I have added a brief development of equations of balance and constitutive relations for the life and migration of locust in a single spatial dimension in Chapter 11.
- Short conceptual and review questions have been added to most of the chapters of the book. They should require no more than a pencil and a piece of paper, and maybe not even that. Answers to these questions are provided in the Appendix.
- There are short answers to many of the end-of-chapter problems in the Appendix. A solutions manual will accompany the book.
- I have changed the sign convention for fluxes. Previously, I had chosen to go with the tradition of electromagnetic field theory where an outward flux is given a positive sign. Now, I prefer to count a flow *into* a system as a *positive* quantity. This leads to two changes: (1) in the laws of balance, the rate of change of a fluidlike quantity equals the sum of the currents (rather than the negative sum); (2) a flux as the surface integral of a current density obtains a minus sign. The convention adopted here should be more convenient for engineering students.

Many of the new aspects and elements have been inspired by a didactics of inquiry based learning which I have been privileged to build up with Georges Ecoffey of the University of Applied Sciences of Western Switzerland and Edy Schütz (Bildungszentrum Uster),[1] partially under a grant made available by the Eduard Job Foundation for Thermal and Chemical Dynamics in Hamburg, Germany.[2] My school and colleagues at the Center of Applied Mathematics and Physics have been supportive in the construction of a studio for introductory physics courses where I have been able to apply new learning materials and tools for the last few years. In particular, I would like to thank Jürg Krieg who has made sure that funds were available, and Arthur Baumann who has been doing much of the actual setting up of the studio. I would like to express my gratitude to Paolo Lubini for editing Chapter 6, Jürg Hosang for end of chapter problems for that same chapter, Georges Ecoffey for editing the entire book, and David Packer and the staff at Springer who have been patient and always very supportive of this project.

Again, my special gratitude goes to my wife Robin who did the language editing of the entire text.

Winterthur, June 2010 *Hans Fuchs*

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[1] See the Website for *Physics as a Systems Science—A Virtual Learning Environment* at http://www.zhaw.ch/~fusa/PSS_VLE/index.html.

[2] See the Website at http://www.job-stiftung.de.

Preface to the First Edition

The last few decades have seen the development of a general approach to thermodynamic theory. Continuum thermodynamics has demonstrated to us how we can build a theory of the dynamics of heat rather than of statics. In this book I would like to transfer what I have learned about the general theory to an introductory level and to applications in the sciences and engineering.

Two elements combine to make this presentation of thermodynamics distinct. First of all, taking as the foundation the fundamental ideas that have been developed in continuum thermodynamics allows one to combine the classical theory of thermodynamics and the theory of heat transfer into a single edifice. Second, didactic tools have been built that make it not just simple, but rather natural and inevitable to use entropy as the thermal quantity with which to start the exposition. The outcome is a course that is both fundamental and geared toward applications in engineering and the sciences.

In continuum physics an intuitive and unified view of physical processes has evolved: That it is the flow and the balance of certain physical quantities such as mass, momentum, and entropy which govern all interactions. The fundamental laws of balance must be accompanied by proper constitutive relations for the fluxes and other variables. Together, these laws make it possible to describe continuous processes occurring in space and time. The image developed here lends itself to a presentation of introductory material simple enough for the beginner while providing the foundations upon which advanced courses may be built in a straightforward manner. Entropy is understood as the everyday concept of heat, a concept that can be turned into a physical quantity comparable to electrical charge or momentum. With the recognition that heat (entropy) can be created, the law of balance of heat, i.e., the most general form of the second law of thermodynamics, is at the fingertips of the student.

The book contains two lines of development which you can either combine (by reading the chapters in the sequence presented) or read separately. In addition to the four chapters which represent the main line, you will find a Prologue, an Interlude, and an Epilogue which discuss some subjects at a somewhat higher level.

The four chapters that form the main body of the text grew out of my experience in teaching thermodynamics as a part of introductory physics, but represent an extension both in content and level of what I commonly include in those courses. The extension mostly concerns subject matter treated in courses on engineering thermodynamics and heat transfer and applications to solar energy engineering. Still, the chapters maintain the style of a first introduction to the subject. Previous knowledge of thermal physics is not required, but you should be familiar with basic electricity, mechanics, and chemistry, as they are taught in introductory college courses. With the exception of one or two subjects, only a modest amount of calculus is used. Chapter 1 provides an introduction to basic quantities, concepts, and laws. Entropy is introduced as the quantity which is responsible for making bodies warm or for letting ice melt, and the law of balance of entropy is formulated directly on the basis of ideas taken from everyday images of heat. The relation between currents of heat (entropy) and currents of energy is motivated along the lines of Carnot's theory of heat engines, yielding a law which makes the development of thermodynamics rather simple. (The relation is proved later on the basis of some alternative assumptions in the Interlude.) Then, some simple applications which do not rely too heavily upon particular constitutive relations are developed. First among them is a treatment of irreversibility and the loss of power in thermal engines, a subject which teaches us about the importance of the rule of minimal production of heat. Chapters 2, 3, and 4 furnish introductions to constitutive theories. The first of these deals with uniform bodies, which respond to heating by changing mechanical or other variables. A simple version of the constitutive theory of the ideal gas is developed, which leads to a theory of the thermodynamics of ideal fluids. In addition, blackbody radiation and magnetic bodies are treated. A short exposition of the concepts of thermostatics exposes the reader to the difference between dynamics and statics in the field of thermal physics. Chapter 3 deals with theories of heat transfer excluding convection. The general form of the equation of balance of entropy for bodies and control systems is given and applied to various cases. Production rates of heat in conduction and radiation are calculated and applied, among others, to the computation of the maximum power of solar thermal engines. In this chapter, continuous processes are treated for the first time in the context of one-dimensional conduction of heat. The radiation field and the issue of the entropy of radiation are discussed extensively, and a section on solar radiation concludes this Chapter. Chapter 4 extends the theory of heat to processes involving the change and the transport of substances. Subjects such as chemical reactions, phase changes, and convection, and applications to power engineering and to heat exchangers form the body of this Chapter. All of these Chapters include a large number of solved examples in the text.

The second track of the book treats thermodynamics in a more advanced and formal manner. The Prologue provides a brief view of a unified approach to classical physics. Except for the first section, which you definitely should read before starting with Chapters 1 – 4, the Prologue presents several subjects of physics at a relatively quick pace, demonstrating the unified approach to dynamical processes which forms the backbone of the entire book. (The concepts are introduced at a more leisurely pace in the main chapters on thermodynamics.) If you wish, you can then try to read the Interlude which introduces the subject of the thermodynamics of uniform fluids on the basis of the caloric theory of heat. This Chapter repeats the subject of part of Chapter 1 and most of Chapter 2 at a higher mathematical level. In contrast to those chapters, the Interlude also provides a first proof of the relation between currents of entropy and of energy, which shows that the ideal gas temperature can be taken as the thermal potential. Finally, the Epilogue takes the first simple steps into the field of continuum thermodynamics, exposing you to the ideas behind the more advanced subjects which have been the focus of development over the last few decades.

If I seem to succeed in introducing you to an exciting new view of a classical subject, the individuals actually responsible for this achievement are the researchers who have developed this field. Carnot, who gave us an image of how heat works in engines, a view which I have taken as the starting point of my exposition. Gibbs demonstrated how to deal with chemical change and heat. Planck's theory of heat radiation still is one of the clearest expositions of the thermodynamics of radiation. Also, there are the researchers who have built continuum thermodynamics, mainly since the 1960s and who have contributed so much toward clarifying the foundations of the dynamics of heat. They deserve our respect for one of the most fascinating intellectual endeavors.

When it comes to applications we nowadays can turn to computational tools which can make life so much easier. Two such tools which I have used deserve to be mentioned—the system dynamics program Stella (High Performance Systems, Inc., Hanover, New

Hampshire), and the program EES (Engineering Equation Solver; Klein, 1991) which provides for extensive thermophysical functions in addition to a solver for nonlinear equations and initial value problems. Also, in the fields of engineering applications, including solar engineering, I have been inspired by such excellent textbooks as those of Bejan (1988), Moran and Shapiro (1992), Rabl (1985), and Duffie and Beckman (1991).

I am grateful to all my friends, colleagues, and teachers who, through their encouragement and support, have contributed toward the writing of this book. Robert Resnick and Roland Lichtenstein of RPI gave me the courage to take up the project. Walter Cohen, Werner Maurer, and Martin Simon read the book and gave me valuable feedback. Heinz Juzi, Heinz Winzeler, and Klaus Wüthrich helped me with discussions of applications, and many more colleagues gave me kind words of encouragement. Most important, however, has been Werner Maurer's friendship and professional companionship in this endeavor. He and I developed the system dynamics approach to the teaching of physics which you will find in this book.

I would like to acknowledge generous grants made available by the Federal Government of Switzerland and my school, which allowed for the development of labs and courses dealing with renewable energy sources, and I would like to thank my thesis students whose work in solar energy engineering has led to many interesting applications included here.

Finally, let me express my gratitude toward all those at Springer-Verlag, who have made the production of the book possible. Thomas von Foerster, Frank Ganz, and Margaret Marynowski turned the manuscript of an amateur madly hacking away on a Macintosh into a professional product. They were very supportive and encouraging, always with an open mind for my wishes.

This has been a long journey. My wife and my daughter have gone through it with me all the way. I would like to thank them for their love and their patience. When my daughter was very little, she asked me if I would dedicate this book to her. I hope it has been worth waiting for.

Honolulu, 1995 *Hans Fuchs*

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INTRODUCTION

FROM METAPHORS TO MODELS OF HEAT

This book is as much about how people understand thermal and other physical processes as it is about thermodynamics itself. Since the approach chosen here to describe and model thermal phenomena probes the roots of imagination and understanding, a few words about human conceptualizations of natural processes might be in place. This should allow me to set the stage for a theory of the *Dynamics of Heat*.

Even though this chapter is called *Introduction*, the material covered is not introductory. I just want to get some philosophy, cognitive science, continuum physics, history, and modeling theory out of the way before starting on the science of heat. You may prefer to start with Chapter 1—or Chapter 4 if you are familiar with the physics of dynamical systems—and come back to these lines at a later time. After you have tried your hand at a dynamical theory of heat, you will be prepared to tell whether or not you agree with my rationale for the conceptualization of thermal phenomena.

I.1 SOME CONCEPTUAL CHALLENGES

Traditional courses treat thermodynamics in a form unlike anything else known in physics. In particular, we are told that it is a theory of the equilibrium of heat and not of how and how fast things happen in real life. This combines with the conceptualization of heat as energy (or a form of energy) and thermal processes as the result of the motion of little particles. The result is a theory that uses strange d's in its equations, does not produce initial value problems as we know them from the rest of physics, and introduces concepts such as exergy, enthalpy, free energy, and Gibbs free energy, we are hard put to distinguish from energy and entropy and from each other.[1]

How did we arrive at such a representation of thermal phenomena? We know that two to three hundred years ago scientists thought of heat as a kind of subtle fluid that goes

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[1] Here's a gem from the Internet: "Entropy is never enthalpy, nor free energy. A system's enthalpy is only entropy change (after DH is divided by T) if it is transferred to the surroundings and no work of any sort is done there in the surroundings. A surroundings' enthalpy is only entropy change (after DH being divided by T) when it is transferred to the system and no work is then performed in the system. Gibbs free energy change, DG, is only considered entropy change (after being divided by T) when no useful work of any kind is done by the heat transfer in the system or in the surroundings." (www.2ndlaw.com/gibbs.html; visited on February 15, 2007.)

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_1,

into bodies to warm them or to cause other changes. The concept is called the *caloric theory of heat*. Around 1820, Sadi Carnot (Carnot, 1824) used this conceptualization to create a theory of heat engines (see Section I.3). In his view, caloric passes from a hot to a cold body without being consumed, thereby producing "motive power." This is like water falling from a higher to a lower point driving a water wheel.

His theory met with some problems. On the one hand, it appears that unlimited quantities of heat can be produced in irreversible processes such as rubbing or burning, whereas the caloric theory of heat assumed that caloric was conserved and could not be produced or destroyed (Fox, 1971). On the other hand, and possibly more important from a formal point of view, Carnot's model predicted that the heat capacities of a simple gas should be inversely proportional to its temperature. This contradicted the result based on a view of heat as the energy of the irregular motion of little particles of the gas. In this model, the capacities of a perfect gas should be constant, independent of temperature.[2]

Rudolf Clausius (1850) solved the problems encountered in Carnot's theory by using the idea of the conversion of heat to work. Some of the heat passing from the furnace of a heat engine to the cooler is "converted" to work—only the rest is passed on to the cooler. So heat and work are interconvertible (in some sense), and since work is a form of energy, so must heat be. Clausius proved the existence of an energy function of fluids which made the First Law a result that went beyond the concept of energy as a mere integral of motion. Heat no longer could be visualized as this thermal fluid responsible for making stones warm, or for expanding air, or for melting ice. In Clausius' theory, both problems of Carnot's model were solved. Heat was not produced in irreversible processes but converted from work, and the "heat capacities" of a simple gas turned out to be constant.

This is the theory that brought us the funny d's, the supremacy of equilibrium over dynamics,[3] and concepts everybody confesses cannot be understood but can only be dealt with in mathematical formalisms. Specifically, standard every-day reasoning about a quantity of heat residing in bodies and flowing into and out of these bodies, does not apply in Clausius' *mechanical theory of heat*. The theory does not provide for a quantity of heat except for the case of a quantity of energy transferred as a result of heating or cooling. Any other use of the word *heat* is forbidden.[4]

From a conceptual and emotional viewpoint, we have paid dearly for the new theory of heat. We know of the problems this conceptualization of thermal processes creates for learners, and everyone else for that matter. Every teacher of physics knows this, and years of research into conceptual difficulties learners encounter with the science of heat have confirmed this. What normal person should be able to understand that the heat that was just transferred into a room by heating is not to be found in the room?

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[2] As Rudolf Clausius put it, "[…] other facts have lately become known which support the view that heat is not a substance but consists in a motion of the least parts of bodies." (Clausius, 1850). See Truesdell (1980) for a discussion of the case of heat capacities.

[3] "The single, all-encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system." (Callen, 1985, p.26). Try to say this about mechanics, or electricity, or fluids.

[4] It has even been suggested to exorcise the word heat from thermodynamics altogether. See Romer (2001): "Heat is not a noun."

Instead of simple conceptual explanations, we are offered words of wisdom concerning the beauty and mystery of entropy—pop philosophy in place of hard science based on how humans conceptualize natural processes (see Section I.2).

We should not and could not criticize traditional thermodynamics just for being arcane and difficult to comprehend if the theory were the only possible one, and if it delivered a fair description of the real world of dynamical thermal phenomena. It is not, and it does not. We know that in a theory of the equilibrium of heat, there are no evolution equations to be formulated and solved—there is no equation analogous to Newton's equation of motion, or to the balance of charge in electric systems. Engines do not run, they operate infinitely slowly. Irreversible processes are recognized but not quantified. And quite importantly, thermodynamics is said to be wholly different from the science of heat transfer.[5] Generations of engineering students have had to take two separate courses, one on thermodynamics, the other on heat transfer, and in each they learned that one field has nothing to do with the other.

So we have two challenges: How to create a complete and unified theory of the dynamics of heat, and how to make it conceptually accessible from the start. The first is being addressed more and more frequently. Indeed, we basically have this theory in the form of continuum physics. There is a forerunner—irreversible thermodynamics—and there are the modern theories in the form of rational thermodynamics (Truesdell, 1984) and extended thermodynamics (Müller, 1985, Jou et al., 1996; Müller and Ruggeri, 1998). And we have many fascinating examples of the application of finite time thermodynamics and thermal optimization in engineering thermodynamics (Bejan, 1988; Sieniutycz and DeVos, 2000).

The second challenge was dealt with early on by Callendar (1911) and again by Job (1972) who pointed out that Carnot's conceptualization can serve us well in creating an accessible representation of thermal phenomena. Caloric—freed from the requirement of conservation—turns into the latter-day *entropy*. The theme was followed up in physics education research and has led to introductory courses based on a unified approach to physical processes that use entropy from the beginning (Falk and Ruppel, 1976; Schmid, 1982, 1984; Herrmann and Schmid, 1983; Fuchs, 1986, 1987a-c, 1996, 1997a,b, 1998; Burckhadt, 1987; Maurer, 1996; Herrmann, 2000, 1998–2010; Borer et al., 2005; Fuchs et al., 2001–2010).[6] Most importantly, in my view, these developments have demonstrated the validity of strong analogical reasoning that allows us to create new and unified representations of well known phenomena.

In the first edition of this book, I produced a uniform systems version of thermodynamics by combining continuum physics with what we had learned from our didactic research:

> Examining the flow of heat in this way makes it clear that the entropy is the fundamental property that is transported in thermal processes (what in lay terms would be

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[5] "At this point it is appropriate to note the fundamental difference between heat transfer and thermodynamics. […] Thermodynamics is concerned with equilibrium states […] heat transfer is inherently a nonequilibrium process […] heat transfer therefore seeks to do what thermodynamics is inherently unable to do […]." (Incropera and DeWitt, 1996, p.12).

[6] An analogous development is taking place in chemistry didactics where the chemical potential is given center stage (Job, 2004; Job and Rüffler, 2011; see also Chapter 4 of the first edition of *The Dynamics of Heat*, 1996).

> called “heat”), and that the temperature is the corresponding potential. The resulting theory of the creation, flow, and balance of entropy provides the foundation of a truly dynamical theory of heat that unites thermodynamics and heat transfer into a single subject. (Tom von Foerster, from the back cover of the first edition of *The Dynamics of Heat*, 1996.)

We now know how to formulate ordinary differential equations for initial value problems in thermodynamics in simple yet practical applications accessible to the beginner in high school or at university.

Clearly, the two challenges are related. Without a conceptual structure similar to the one that gives us theories of dynamics in fluids, electricity, or motion, we cannot simply come up with a dynamics of heat. Let me therefore discuss some recent investigations into every-day conceptualizations of physical processes that demonstrate how our imagination produces useful concepts for a formal science.

I.2 COGNITIVE STUDIES OF CONCEPTUALIZATIONS OF PROCESSES

Not so long ago I was told the following story (Sassi, 2006). Little Alex came home from kindergarten. He told his grandmother that the teacher had said they should close the door if they did not want cold to come in. Now his grandmother asked Alex what cold was. He said that cold was a snowman. A snowman was very cold and if he hugged Alex, the boy would also get cold and might get sick. Alex and his grandmother were outside and decided to build a snowman. When his grandmother wanted to build a big one, Alex said that a big snowman would be so cold it could even kill young Alex. He thought it would be better to build a small snowman. Finally, his grandmother wanted to know what he thought heat was. Alex said, heat was a dragon. He could play with little dragons, they were not so hot and dangerous, but a really big dragon would be so hot and strong, its fire could kill the boy.

Now compare this to the description of the concept of heat by the experimenters of the Accademia del Cimento in 1667 who tried to determine the power of heat and cold. According to Wiser and Carey (1983), their concept included the aspects of “substance (particles), quality (hotness), and force.” These elements are found in Alex’ story as well—size, coldness or hotness, and the power to harm the boy. Now turn your attention to a completely different phenomenon such as justice. If you apply methods developed in linguistics to how we speak about this concept, you will find a closely related structure, an *experiential gestalt* having aspects of quantity (“Let justice flow like water,” Martin Luther King), quality or intensity (“He has a horrid history and deserves strong justice”), and power (“The healing power of justice”).

These are examples of an understanding of processes which appears in many areas of human experience. My knowledge of the structure of classical physics suggested to me that certain imaginative structures must be recurring in the conceptualization of phenomena. I found background material on schematic structures of human understanding in modern cognitive science and linguistics (Arnheim, 1969; Lakoff and Johnson, 1980, 1999; Johnson, 1987, 2007; Lakoff, 1987; Talmy, 2000a,b; Hampe, 2005). In short, physics, cognitive science, Alex’ story, and many examples of how people speak about processes led me to identify what I now call *force dynamic gestalts* (Fuchs, 2007). The human mind seems to generate these perceptual gestalts that have at least the following three aspects: *quantity* (size), *intensity* (quality), and *force* or *power* (the latter stand for forms of causation). The aspects are rooted in image schemas (such as fluid substance, scale and verticality, direct manipulation, and others) that are projected metaphorically[7] onto the particular phenomenon under consideration. For example, verticality is projected onto the concepts of brightness, temperature, or pressure (brightness goes up, temperature is low, etc.) which are created from polar schemas of light and dark, hot and cold, strong and weak.

There are additional schemas related to force dynamic gestalts: balance (or equilibrium), letting, forcing, hindering, preventing, etc. In short, conceptual structures identified in cognitive semantics for a wide range of fields of human interest also apply to the basic conceptualization of natural phenomena such as heat, fluids, electricity, motion, or chemical change.

Clearly, quantity (size), intensity, and power are intertwined in Alex' description of the properties of snowmen and dragons. When I saw that we create the same gestalt in conceptualizing phenomena such as justice or pain, market or information, I became convinced that Alex' story was more than just an offspring of an unchecked imagination of a little boy, an imagination that has to be reigned in later in life if the child is to succeed in school. It testifies to a structure of figurative thought that is foundational to human understanding of nature. In terms of modern cognitive science, what we see here is an experiential gestalt whose aspects are structured through metaphoric projections of just a few image schemas. Since the same gestalt is constructed for different phenomena such as fluids, electricity, heat, and motion, these fields become similar to each other in our mind, which allows us to apply analogical reasoning—understand one field in terms of the structures of another.

Does this mean that anyone can come up with formal descriptions of thermal or other physical processes effortlessly? Not quite. Children and laypersons do not commonly distinguish between the quantity and the intensity of heat, nor is it easy for us to see the difference between intensity and power, or quantity and power.[8] An investigation of the metaphoric base of the gestalt of heat shows that its aspects are not easily kept apart in common sense reasoning.[9] Therefore, one of the most important goals of education must be the differentiation of these aspects in the course of education.

What I have outlined here shows that common-sense conceptions of nature may be

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[7] Simply put, a metaphor is a device of figurative thought in which knowledge of a source domain is projected onto a target domain. In cognitive science, metaphors are no longer considered just embellishments of language or a rhetorical device. They are given conceptual status, reflecting figurative structures of thought (Lakoff and Johnson, 1980; Koevecses, 2000; Evans and Green, 2006). It is important to distinguish between a linguistic metaphorical expression ("heat escapes the room") and the actual underlying metaphor HEAT IS A FLUID SUBSTANCE. Note that the metaphors I am mentioning here are of a simple, foundational nature (in fact, they are part of conventional language which does not easily let us recognize them as such). These structures are more important to me in the present context than the more obvious metaphors such as THE ATOM IS A SOLAR SYSTEM or A CELL IS A FACTORY. I believe that science is metaphorical at its base, not just at the surface where we try to make a person understand a complex subject by representing it with the help of vivid language and comparisons.

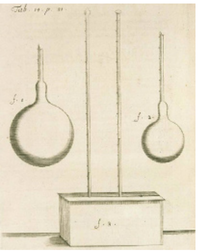
[8] Clausius does not distinguish between the quantity and the power of heat. Trying to fool the human mind exacts its price—entropy comes in through the back door and takes its revenge (Fuchs, 1986).

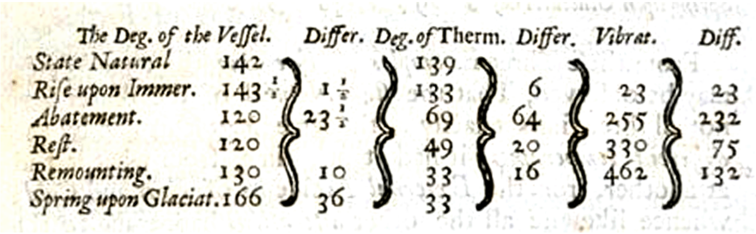
[9] For example, we connect quantity and intensity (verticality) in the metaphor MORE IS UP.

much more useful than has been realized up until now. Let us see how these figurative structures of thought made their appearance in the course of the early history of thermal phenomena and thermal physics.

I.3 FROM THE ACCADEMIA DEL CIMENTO TO SADI CARNOT

In 17th century Florence, a group of experimenters who called themselves the Accademia del Cimento studied thermal and other processes (Magalotti, 1666). They reported on their experiments many of which were designed to investigate the power of cold (and heat). They stuck a bulb with a long neck (called the *Vessel*) filled with water or other liquids to be frozen, into a box with ice and salt (Fig. I.1). Then they placed a second such bulb containing alcohol in the ice; this device was their *Thermometer*. They observed the levels of the liquids in the Thermometer and in the Vessel while measuring how long certain steps such as *Rise upon Immersion*, *Abatement*, *Rest*, etc. took and reported the results (Fig. I.1): Degrees of Vessel, Difference, Degrees of Thermometer, Difference, Vibrations (of the clock), and Difference. Basically, they measured the speed at which processes were running.





	The Deg. of the Veſſel.	Differ.	Deg. of Therm.	Differ.	Vibrat.	Diff.
State Natural	142		139			
Riſe upon Immer.	143½	1½	133	6	23	23
Abatement.	120	23½	69	64	255	232
Reſt.	120		49	20	330	75
Remounting.	130	10	33	16	462	132
Spring upon Glaciat.	166	36	33			

Figure I.1: Experimental arrangement set up by members of the Accademia del Cimento to measure the power of cold (left). A table with results of their measurements (right).

To the modern observer, this looks and sounds rather strange. The reason for this is not just that they put the thermometer side by side with the probe in the ice to measure the temperature of the freezing water, but also because of something we don't do any longer (or rather have not done for a long time): we do not use a clock to time such phenomena. Speed is of no importance to us in traditional thermodynamics.

I do not want to say that the Experimenters had anything resembling a theory of thermal processes.[10] What is interesting is their language combined with their actions. As mentioned above, a cognitive scientist might say that they made use of the force dynamic gestalt of heat, and they searched for the power of cold or heat in the dynamics of the processes. They did not carefully distinguish between the separate aspects of this gestalt—learning how to do this was going to take another 150 years.

In the years leading up to Sadi Carnot's and his contemporaries' work, quantities of heat were finally distinguished from the measure of hotness. Joseph Black is credited with making this distinction clear by introducing the concepts of latent and specific heats. The concepts were created on the foundation of the caloric theory of heat.

By the time Carnot created his theory of heat engines, some of the fog was clearing,

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[10] For a criticism of their work in the light of traditional thermodynamics, see Wiser and Carey (1983).

and formal mathematical models dealing with examples of thermal processes had been produced (see Truesdell, 1980). Among these were a theory of heat conduction and a model of adiabatic processes in gases which was used to explain the observed speed of sound. Again, all of these achievements were based on the assumption that heat was some kind of imponderable fluid.[11]

Understanding of heat engines was still limited, so Carnot proposed to answer questions regarding the *Motive Power of Fire, and Machines Fitted to Develop that Power* (this is a paraphrase of the title of his book). To quote Carnot (1824, p. 3, 6):

> Every one knows that heat can produce motion. That it possesses vast motive-power no one can doubt, in these days when the steam-engine is everywhere so well known.
>
> To heat also are due the vast movements which take place on the earth. It causes the agitations of the atmosphere, the ascension of clouds, the fall of rain and of meteors, the currents of water which channel the surface of the globe, and of which man has thus far employed but a small portion. Even earthquakes and volcanic eruptions are the result of heat.
>
> The phenomenon of the production of motion by heat has not been considered from a sufficiently general point of view. […] A [complete] theory is evidently needed for heat engines. We shall have it only when the laws of physics shall be extended enough, generalized enough, to make known beforehand all the effects of heat acting in a determined manner on any body.

Since Carnot's time, it has become evident that the action of heat can effect more than just motion. Heat drives many other processes, such as electric and chemical ones. We take these phenomena as a sign of the interrelation between different classes of physical processes.

Heat can be used to do things; it can drive engines; it is an agent for effecting things. In other words, heat can do work. Does this mean that heat is some sort of work? The answer should be "no." Water can also be used to drive water wheels and turbines. Does this make water some sort of work? Certainly not. Similarly, electricity, i.e., electric charge, can be used to do work, but it is not work.

The gestalt with its aspects of quantity, intensity, and power must have been present in Carnot's mind. Carnot created a vivid image of the *Power of Heat* by using waterfalls as an analogy for the operation of heat engines. Doing so, he produced the basis of a formal differentiation of the aspects of the gestalt (Carnot, 1824, p. 15):

> According to established principles at the present time, we can compare with sufficient accuracy the motive power of heat to that of a fall of water … . The motive power of a fall of water depends on its height and on the quantity of the liquid; the motive power of heat depends also on the quantity of caloric used, and on what may be termed, on what in fact we will call, the *height of its fall*, that is to say, the difference of temperature of the bodies between which the exchange of caloric is made. In the fall of water the motive power is exactly proportional to the difference of level between the higher and lower reservoirs. In the fall of caloric the motive power undoubtedly increases with the difference of temperature between the warm and the cold bodies; but we do not know whether it is proportional to this difference.

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[11] Truesdell showed that the assumption regarding the nature of heat is not necessary for the theory of adiabatic motion (Truesdell, 1980). However, the scientists who created it used the caloric theory.

Quantity, intensity, and power of heat are distinguished, and their relation is made formal—ready to be put in the form of an equation. Just as water falls from a high level to drive a turbine, after which it flows out of the engine at a lower level, heat is imagined to fall from a high temperature to a lower one, thereby driving the heat engine (Fig. I.2), and then flowing out at lower temperature. The principle of operation of heat engines is in accordance with this image. Steam takes up caloric (heat) from a burner, and passes through the engine where it effects motion, just to flow out again and to give up its heat (caloric) to a condenser. As Carnot put it (1824, p. 7):

> The steam is here only a means of transporting the caloric … . The production of motive power is then due in steam-engines not to an actual consumption of caloric, but to its transportation from a warm body to a cold body.

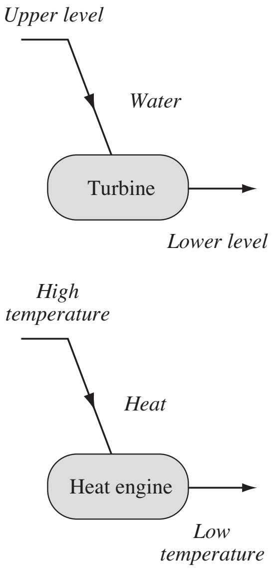

Figure I.2: Hydroelectric and thermal power plants are structurally comparable. Water drives a turbine by falling from a higher to a lower level. Heat drives a heat engine by "falling" from a higher to a lower thermal level.

We know today that we can indeed explain the motive power of heat in terms of these images. There is a deep similarity between different types of physical processes. Hydroelectric power plants and heat engines are two examples which serve to drive home this point (Fig. I.2).

Those of you who already know thermodynamics may have noticed that Carnot's heat or caloric can be reinterpreted as the modern-day entropy. We simply have to make sure that we allow for caloric to be produced in irreversible processes. For those of you new to thermal physics, do not let yourselves get confused by an arbitrary, artificial word created by Rudolf Clausius in the 1860s. For us, entropy is the child's heat, the layperson's heat substance, or better, Carnot's caloric—suitably extended by the assumption that it can be produced but not destroyed.

The similarity observed here is a result of the imaginative power of the human mind represented by force dynamic gestalts. There is a branch of physics which makes use of this conceptualization in a broad manner, namely, *continuum physics*. Let me briefly list the basic characteristics of this approach to the description of physical and chemical phenomena.

I.4 A UNIFIED APPROACH TO PHYSICAL PROCESSES

Everything flows. Water and air flow on the surface of the Earth, where they create the multitude of phenomena we know from everyday life. Winds can impart their motion to the water of the oceans, and in a far-away place, this motion can be picked up again through the action of the waves. These processes are maintained by the radiation pouring out from the surface of the sun; light flows from there through space, and some of it is intercepted and absorbed by our planet. Both in nature and in machines, heat is produced and transported from place to place. In electrical machines, we make electricity flow in an imitation of its flow in the atmosphere; in reactors, chemical substances flow while at the same time undergoing change. Today, we even see life as governed by flow processes.

The sum of these observations can lead us to one of the most general description of nature known today. There are a few physical quantities which can flow into and out of systems, which can be absorbed and emitted, and which can be produced and destroyed. Electrical charge is transported in electrical processes, and mass and substance flow in gravitational and chemical phenomena, respectively. In continuum mechanics, motion is seen as the exchange of linear and angular momentum. Thermal physics is the science of the transport and the production of entropy. One of the great advantages of this description of nature is that it relates the different phenomena, which leads to an economical and unified view of physical processes. It turns out that classical continuum physics is a precise method of expressing this point of view for macroscopic systems.

What is this unified approach to physics? First, we have to agree on which physical quantities we are going to use as the fundamental or *primitive* ones; on their basis other quantities are defined, and laws are expressed with their help. Second, there are the fundamental *laws of balance* of the quantities which are exchanged in processes, such as momentum, charge, or amount of substance; we call these quantities *fluidlike*.[12] Third, we need particular laws governing the behavior of, or distinguishing between, different bodies; these laws are called *constitutive relations*. Last but not least, we need a means of relating different types of physical phenomena. The tool which permits us to do this is energy. We use the *energy principle*, i.e., the law which expresses our belief that there is a conserved quantity which appears in all phenomena, and which has a particular relationship with each of the types of processes.[13]

The most basic constitutive relations result from the metaphoric interpretation of the intensive quantities associated with processes—speed with momentum, electric potential with charge, or temperature with entropy. These quantities are levels—remember, they are described as being high or low by virtue of the projection of the schema of verticality onto the polarity which is constructed by our perception. An intensity results from the containment of a fluidlike quantity in a system: Pressure goes up if more liquid or gas is put into a container. This we call a *capacitive relation*. Differences of intensities are conceptualized as *driving forces* of processes. So the electric potential difference serves as a driving force for the flow of charge through a conductor, and a chemical potential difference is visualized as the driving force for the diffusion of a substance through a material. Such relations we call *resistive characteristics*.

The notion of levels and level differences as driving forces is instrumental also for understanding the role of energy in physical processes. We simply relate the power of processes to driving forces and flows, as Carnot did. This is the starting point for my approach to the energy principle used throughout this book (Chapter 2).

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[12] Falk and Herrmann (1977-1982), who started a unified approach to high school and university physics in their didactic research, coined the term *substancelike*. I prefer *fluidlike* since we transfer the image of fluids into our formal descriptions of processes. The Merriam-Webster Online Dictionary defines *fluidlike* as a "substance (as a liquid or gas) tending to flow or conform to the outline of its container." This is not bad for our purpose. Momentum, charge, or entropy flow and fill space or materials in space. We have to add the notion that some of these quantities can be produced and/or destroyed.

[13] This is slightly different from the standard approach in continuum physics (or continuum thermodynamics). Taking the usual approach of continuum mechanics, one formulates laws of balance of momentum, angular momentum, and mass, and complements this with the energy principle. Then constitutive relations are added. Thermal processes are treated as a somewhat different breed. One starts with the already known equations such as for momentum and energy, formulates constitutive laws for the thermal phenomena, and finally adds the law of balance of entropy as a special relation. This does not bring out the deep analogy between thermal and the other kinds of processes I am going to use as my starting point. I take the balance of entropy (the quantity of heat introduced above) as a basic relation alongside those for momentum, charge, or amount of substance. Energy is the special quantity in this approach.

Models are created from combinations of laws of balance and constitutive relations. Since we want to compare the predictions of our models with data from experiments, we need results for the most easily measured quantities such as speed, density, pressure, or temperature. This means that we have to solve for these quantities while eliminating the rest. The "undesirables" are mainly the fundamental fluidlike quantities—charge, momentum, entropy (our modern version of caloric). For example, to study the conduction of heat, one formulates the law of balance of entropy and adds constitutive laws for the storage, flow, and production of entropy. The constitutive laws introduce temperature. Then we eliminate entropy and obtain a *field equation* for temperature which we solve.

This is rather fascinating. We need speed, density, pressure, and temperature to relate our models to the world, and mostly we do not care much about the fluidlike quantities. Who cares about entropy, or momentum? We want to know how warm it is, and how fast a body moves. But we cannot create models, i.e., understand the world, without the help of the quantities which seem to be pure constructs of our imagination.

Continuum physics teaches us these important things about the structure and the role of models of processes. Fortunately, there is a strongly simplified version—a subset—of continuum theory from which we can learn about these things. This version is made up of the *uniform dynamical models* of physical processes—including thermal and chemical ones—which we are going to study for much of the first half of this book.

I.5 DYNAMICAL MODELS OF HEAT

So how do we construct dynamical models of thermal phenomena? Just as we do in (introductory) mechanics, or when we describe the charging or discharging of capacitors. To model a ball falling straight down in air, we formulate the law of balance of momentum for the ball. There are two momentum transports to consider: one due to gravity, the other resulting from friction between the ball an air. Then we express the momentum flows (the forces) by appropriate constitutive laws (force laws), and we formulate the relation between momentum and speed of the body. The constitutive relations introduce the speed of the body. We rearrange the equations so that we end up with an initial value problem for the speed of the ball which we then solve.

Let us transfer this method to thermodynamics. Consider the cooling of hot water in a thin walled can, placed in a room and stirred with the help of a magnetic stirrer. We formulate the law of balance of entropy (heat, caloric) for the body of water. The entropy changes because of cooling, i.e., because of the transport of entropy out of the water and into the room. Moreover, we have to take into consideration the production rate of entropy due to friction between the magnetic bar and water. Now we need constitutive laws for the temperature–entropy relation of water, an expression for the entropy flow from the hot water to the cold environment, and one for the production rate of entropy due to stirring.[14] The material laws introduce the temperature of the body

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[14] Here we use the energy principle to derive the missing expression. How much entropy is produced in an irreversible process depends upon the quantity of energy dissipated, and upon the temperature at which dissipation is taking place. In thermal design in engineering, it has become customary to express entropy production rates by combining laws of balance of entropy and of energy with appropriate constitutive laws (Bejan, 1988, 1996).

of water. The model has now been cast in the form of a set of differential and algebraic equations. They can be rearranged to yield a single initial value equation for the temperature of the water which we solve.

If it is so simple to produce dynamical models in thermodynamics, why is it not standard practice to do so in physics? The answer has to do with conceptualizations of processes and with basic philosophy of what a model is and what it can do. Here is an example of a problem that has vexed students of thermal physics. Consider a cold block of copper submerged in hot water. In a first step, we would write the laws of balance of entropy for water and copper, and introduce two temperatures, one for water, the other for copper. This means we imagine homogenous bodies having a certain entropy and a certain temperature, capable of absorbing or emitting entropy. Now the entropy flow is between the two bodies whose changes are being considered in the model. Since entropy transfer from a hot to a cold body is irreversible, we have to add an entropy production term to our equations. Moreover, the copper block should be considered an inhomogeneous body between whose parts entropy flows—and again entropy must be produced.

Upon closer inspection, this situation turns out to be anything but trivial from a conceptual viewpoint. I introduced a single temperature of a body as if it were normal for a physical system to have the same temperature throughout. Thermal processes cast a glaring light upon the problem of uniform situations. Normally, when heat (entropy) flows, temperatures change from point to point, which makes it necessary to set up a continuum theory of nature. So, where does this leave us with our desire to learn about thermal processes in the simplest possible settings?

I.5.1 A Continuously Variable World or Eternal Rest?

Objects and systems do not only change with time. Their properties also vary from point to point in space. The point masses of mechanics certainly are not an example of how things are in nature. The electrical capacitor which we describe in terms of a single value for its voltage or its electrical field does not even exist. While bodies move they also may deform, which can make them nonuniform. When air rushes into a vacuum such as in free expansion, we are confronted with a situation which makes it impossible to speak of *the* air pressure.

Thermal phenomena present us with more examples. Experience with the world around us demonstrates most clearly that uniform situations do not exist in general. The temperature never is the same at every point in a body. The Earth's atmosphere is far from a uniform state, and so are our homes and our bodies. When we heat a stone in the Sun or air in a cylinder, heat (entropy) will gradually spread through the system leaving parts closer to the heat source hotter than those further from it. Therefore, the description I just used seems to be utterly unrealistic.

We might think that it should be possible to select parts of bodies small enough for spatial uniformity to prevail to a significant degree. We could attempt to base our description of nature on such systems, from which we would build the world at large. However, this turns out to be impossible: changes of temperature from location to location are required if thermal processes are to take place at all. Heat does not flow without a temperature gradient, not even in the tiniest part of a body. Inevitably, this leads to the production of heat. Thermal processes are dissipative as a matter of fact, leaving us between a rock and a hard place.

You may object to this stark analysis and insist that situations exist in nature in which physical systems can be described as spatially homogeneous. Again, entropy tells the story. If we leave two bodies at different temperatures in contact for a long enough time, their hotnesses will eventually be the same. If we insulate the bodies from the environment we can even maintain this condition over a long period of time without significant change. The air which undergoes free expansion will settle down eventually, making the pressure and temperature uniform throughout. Here, you will say, are cases which we should be able to investigate successfully if we are looking for simple situations.

There only is one problem. The examples provided have nothing to do with *dynamics*. They are cases of eternal rest or, put more prosaically, of *equilibrium*. It seems we must choose between a dynamical world which is too difficult for us to describe, and a simpler, but less interesting, static one.

I.5.2 Uniform Heating in Thermal Superconductors

There must be a way out of this dilemma. After all, we construct theories of mechanical and electrical systems which we describe in simple ways using the notion of spatial uniformity. We calculate the behavior of electrical circuits by assuming them to be composed of discrete elements each of which can be modeled using a few physical variables assumed to have the same values at every point. We model the motion of bodies in the simplest terms, forgetting about spatial inhomogeneity. Ideal pendulums, for example, are points which swing at the end of massless strings through frictionless space. We are quite happy with such simple theories, and we do not let ourselves become unduly worried about the complexities of the real world. After all, the ideal models have an important story to tell despite their shortcomings.

Well, then, let us look for and construct a model of spatially uniform bodies which can undergo thermal processes. How could we conceive of *bodies which remain uniform while they are being heated or cooled*? Obviously we require the spatial variation of temperature in a body to vanish while heat is allowed to flow through it. Carnot imagined bodies which let heat pass easily. The situation he described in such simple words is no stranger to us in other fields of physics. In electricity, we build circuits using wires which “let electricity pass easily,” and we do not blink an eye when we set their resistances equal to zero. In fact, we know of a perfectly modern phenomenon which lets us support the assumption of ideal wires, namely *superconductivity*. We simply take the wires as being *superconducting*: they let charge pass easily; the potential difference across their length is zero; and they do not produce any entropy.

What is the thermal equivalent of electrical superconductivity? It is a conductor where entropy does not require a temperature difference to spread from one point to another. Expressed differently, this is a material having zero thermal resistance. If we let the thermal resistance vanish while the flow of entropy is kept constant, the rate of production of entropy will go to zero as well. A body working according to this prescription may very well be said to be a *thermal superconductor*.

Other ways of heating bodies may lead us to the same conclusion, namely that it is not forbidden to construct models of uniform heating. Imagine many tiny electrical heaters distributed uniformly through a body of water emitting the entropy they create at an equal rate into every part of the body. Another form of evenly distributed sources of entropy is encountered in the absorption of radiation in an almost transparent body.

Radiation from the Sun is absorbed by a few cubic meters of air in our atmosphere at just about a uniform rate. In either case, we may model the actual process as one in which the temperature of the body remains uniform all the time.

I.5.3 Models and Truth

Are uniform processes realistic? It is important to realize that it does not matter whether such bodies and circumstances exist in nature precisely as I have described them. They certainly may exist as models in our theories. They are comparable to ideal wires and ideal pendulums. Just like these simple objects (which cannot be found in nature either), thermal superconductors and evenly spread sources of entropy are the building blocks of a theory of dynamics, this time of the dynamics of heat in uniform bodies. In fact, despite all the factors which we are ignoring, this model leads to important results: bodies undergoing uniform thermal processes approximate many real cases rather well. The idea of the change of a body through homogeneous states is an important ingredient of classical thermodynamics. All we have to do now is to investigate the consequences of such a far-reaching assumption.

Physics is not a science that creates words or concepts that have a direct, one-to-one relation with the world out there.[15] We have already seen that certain quantities such as momentum or entropy occupy a special place in the inventory of human concepts. They are absolutely necessary to talk about nature, to understand it, and to formulate models, but we do not really need their values as we need those of speed and temperature to compare our models with reality. We may very well wonder whether or not these quantities exist out there. Certainly, these concepts demonstrate how human imagination works. We imagine fluids and levels, and the force or power of phenomena. Armed with these schemas and their metaphorical projections, we create stories of how nature works. In science, we have learned how to make the stories formal, i.e., create mathematical models that can be simulated and whose results can be compared with data of phenomena observed in the real world.

I.6 AN OVERVIEW OF THE BOOK

I have divided the book into four parts. Part I discusses hydraulic, electric, and some mechanical processes with the goal of learning how to create simple system dynamics models. In Part II, I introduce thermal and chemical phenomena which will be modeled using the idea of uniform dynamical systems. These models will be formalized and extended to spatially continuous situations in Part III. Finally, in Part IV, a number of applications of thermal and chemical physics will be treated that require the more formal tools made available in Part III.

This book starts with fluid, electric, and rotational phenomena which are conceptualized as resulting from the storage and flow of fluids, electrical charge, and angular momentum (spin), respectively. Then we discuss a general theme: the role of energy in physical processes (Chapter 2). Finally, Chapter 3 extends the discussion to examples

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[15] David Hestenes and I have both discussed the question of the nature of models in the light of modern cognitive science and linguistics (Hestenes, 2006; Fuchs, 2006, 2007).

of translational motion; here, we deal with the transport and storage of momentum. There are several reason for having this part in a book on the dynamics of heat. If we want to model thermal dynamical processes in analogy to how this is done in other fields, we first have to get to know these fields from a systems perspective. Secondly, we need to understand energy in physical processes from a generalized and unified viewpoint. The traditional treatment of the energy principle is not exactly helpful in this respect. I will introduce process diagrams that visualize flows, potentials, power and energy currents, in single systems and in chains of systems. These diagrams can be used as tools in process design (Tyreus, 1999, gives an example in control engineering).

The next six chapters are devoted to an introductory exposition of dynamical thermal and chemical phenomena. With a few exceptions, I will limit the discussion to uniform models. Naturally, if we divide a system into enough uniform parts, we may still get very useful models—certainly good enough for many applications in the sciences, medicine, engineering, and ecology.

Chapter 4 introduces us to hotness, heat (entropy), and energy, and their relation, using simple systems such as water cooling in the environment, two bodies in thermal contact, or (thermoelectric) heat pumps and heat engines. These examples are well suited to the study of basic thermal concepts and for learning how to set up our first dynamical models. The treatment will be extended to substances undergoing phase changes, and to the dynamics of simple fluids such as the ideal gas and thermal radiation (Chapter 5).

Chemical processes—the transport and the reaction of substances—are intimately linked to thermal ones, so it is important to take a closer look at them. In Chapter 6, I will deal with diffusion, solutions, and simple reactions. Concepts—amount of substance and the chemical potential—will be motivated and dynamical models will be set up. Parts of this theme will be important when we take up the transport of heat in Chapters 7 and 8. Finally, in Chapter 9, entropy production minimization will be applied to some interesting examples. This is a particularly useful method of thermal design which leads to models of optimal processes in engineering and in nature.

Chapters 10–12 make up Part III. They detail the construction of a formal theory of the dynamics of heat for uniform and for spatially distributed phenomena. The latter lead to ideas and tools needed for continuum thermodynamics and radiative transfer.

The applications discussed in Part IV deal with conductive and coupled transports (Chapter 13), convective heat transfer (Chapter 14), and phase changes and mixtures and their application to engines and power engineering (Chapter 15). The last chapter describes solar radiation (Chapter 16). The chapters in this part develop more detailed constitutive theories than those encountered in Part II of the book.

Throughout the book, I will use the images and the language of continuum physics as the main tool—to me, continuum physics provides the best example of *images of change* that grow from the basic structures of figurative thought discussed in this Introduction. In this way, I hope to prepare the ground for the approach to thermodynamics which you will find here and in modern treatises of this subject that go beyond what I do here. I believe you will find it advantageous to draw comparisons between different fields of physics and make use of analogical reasoning as often as possible during your journey through thermodynamics.

PART I

PROCESSES, ENERGY, AND DYNAMICAL MODELS

CHAPTER 1

STORAGE AND FLOW OF FLUIDS AND ELECTRICITY

In this chapter, hydraulic and electric phenomena will be introduced and described with concepts known from the physics of dynamical systems and processes. We start with fluids in systems of tanks, pipes and pumps, and extend the description to electrical processes by making use of analogical reasoning. Dynamical models will be constructed that share the same underlying structure even though the phenomena are not at all alike—at least not superficially. The form of the conceptualization, and the tools used to express it, are the same as those used to create models of mechanical systems (Chapter 3). They will be used to build a theory of the dynamics of heat in Part II.

1.1 PHENOMENA AND MODELS IN FLUIDS AND ELECTRICITY

We all are familiar with the flow of water in simple settings, such as the filling or discharging of tanks through pipes. By looking at some special examples, we will be able to identify the elements of a physical theory which allow us to calculate such things as the current of water through a pipe, the pressure at various points in the fluid, the storage of water and associated values of pressure, and the time required to discharge a storage element. Beyond the immediate application, the analysis will tell us that the description of systems and processes is similar to what we know from electricity. By comparing hydraulic and electrical systems, we shall learn about the importance of analogies between different fields of physics.

Fluids and electricity demonstrate most clearly how humans conceptualize processes. *Fluidlike quantities* that are stored and can flow, and differences of their intensities which I interpret as a kind of *tension* or *driving force*, are the basic concepts. In this section, processes of the creation and the equilibration of such driving forces demonstrate how we perceive similarities in otherwise dissimilar phenomena.

1.1.1 Differences, Driving Forces, and Flows

Communicating tanks. Consider two cylindrical tanks connected by a hose at their bottoms, and filled with some oil. We let the oil flow from one tank into the other and measure the fluid levels in the tanks as functions of time (Fig. 1.1).

It turns out that the level of oil in one of the tanks decreases while the other level increases. This is so since the oil flows from where the level is higher to where it is lower. The shape of the measured curves tells us that the process runs fast at the beginning,

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_2,

slows down and comes to a standstill when the levels have become equal (Fig. 1.1, right). We say the system has reached *equilibrium*. There is *dynamics* as long as we have a difference of levels in the two tanks—the level difference is conceptualized as the *driving force* of the flow of fluid.

Note that the final common level is not the average of the initial levels if the tanks have different cross sections (Fig. 1.1). This demonstrates that levels become equal, and not quantities of liquid.

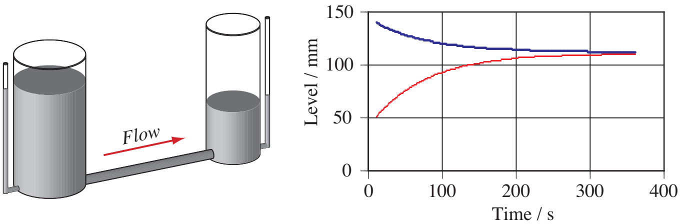

Figure 1.1: Two communicating tanks connected by a pipe. Oil is allowed to flow from one tank into the other. The process runs until the oil levels have become equal.

A closer look at the flow of fluids from one storage element to another shows yet another important aspect of these phenomena. If you fill one of the tanks with oil having a somewhat higher or lower density, the final levels in the tanks will not be the same—even though the flow process has stopped. If we maintain that this is due to the fact that the driving force of the process has become zero, the driving force cannot be measured by the difference of levels of liquids but rather by pressure differences.

Communicating balloons. A third experiment clarifies the situation. Instead of tanks, let us use toy balloons filled with air at different pressures. The balloons are allowed to communicate. If we measure the air pressure in the balloons as functions of time, we see that pressures equilibrate (Fig. 1.2) whereas quantities of air or levels do not (there are no levels of air to speak of in this experiment). In summary, the three cases described above tell us that we can *interpret pressure differences as driving forces of flows of fluids*.

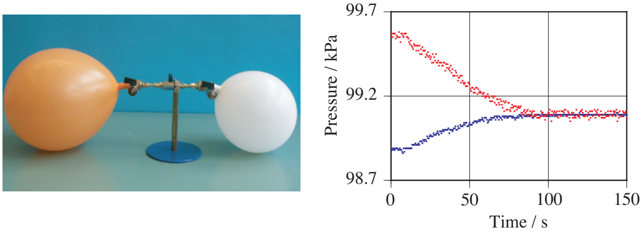

Figure 1.2: Communicating toy balloons demonstrate that pressure equilibrates. Pressure differences are interpreted as the driving forces of the flow of fluids.

Two capacitors in an electric circuit. In a circuit having two electric capacitors with a resistor between them (Fig. 1.3), we can observe a process which demonstrates similar behavior. We charge the capacitors to different voltages in the open circuit, close the circuit and measure the electric potential differences (voltages) as functions of time. We get curves analogous to the ones in the diagrams of Fig. 1.1 and Fig. 1.2—see Fig. 1.3. The interpretation of this phenomenon is analogous to that of fluid processes, and it is well known from electricity. We imagine a quantity responsible for electric processes—compared to quantity of fluid—which we call *electric charge*.

This quantity is said to flow from a place having a higher electrical intensity—called *electric potential*—to one having a lower value of intensity. The process stops when the potential differences across the capacitors have become equal. Note that a potential difference has its own name; it is called *voltage* (the German word for this is *tension*). Observations like the one described here lead us to *interpret electric potential differences (voltages) as driving forces of the flow of electric charge*.

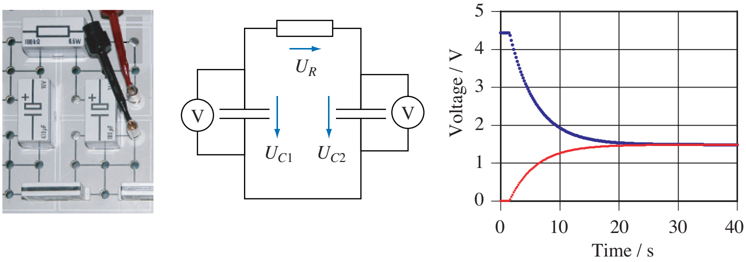

Figure 1.3: Two capacitors in a circuit with a resistor. There is an electric potential difference between the capacitors which spontaneously decays in the closed circuit. Electric potentials equilibrate.

If differences, i.e., driving forces, decay spontaneously as we have seen in these experiments, they have to be reestablished if they are supposed to again make something happen. In nature, on our planet, this works mostly through the action of solar radiation. Chemical and thermal differences are created which in turn create pressure and gravitational differences that drive the oceans and the atmosphere. As long as the Sun shines on us, these vital tensions can be maintained.[1] In engineering we build devices that either set up differences or make use of them.

Driving charge apart. A simple electric experiment shows how this can work in technical settings. Add a battery to the circuit having two capacitors and a resistor (see Fig. 1.4, left). Initially, the devices are uncharged, the electric potential differences across the capacitors are zero: we have electrical equilibrium. If we now connect the battery, i.e., close the circuit, the potentials of the capacitors are driven apart—a potential difference is established (Fig. 1.4, right).

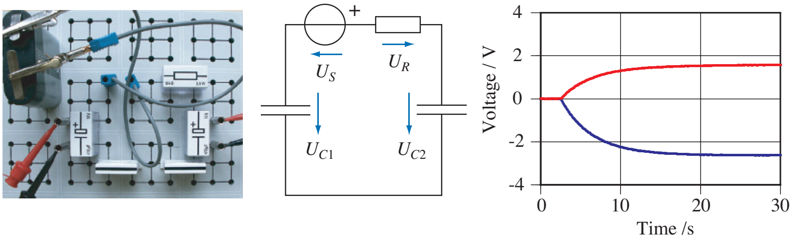

Figure 1.4: Two capacitors in a circuit with a resistor. Here, a battery (circle with plus sign) is added to the circuit. The battery establishes a potential difference between the capacitors.

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[1] In old mythic cultures like Egyptian and Babylonian, people seem to have captured this understanding in their cosmologies. The world begins with a separation of the sky from the earth. In Egypt, it was the god Shu (air) that supports Nut (heavens) from falling to Geb (earth). In Babylonian mythology, it was the wind that separated heaven and earth. Dynamics is rooted in the tension between the poles of the polarities that govern nature and society.

Differences beget differences—there has to be a potential difference in the battery to make that device establish an electric potential difference. This initial tension is chemical in nature. There are chemicals in the battery that react as a result of their innate chemical difference. Later, in Chapter 6, I will take up the issue of chemical processes and formalize the idea of chemical differences by introducing the notion of *chemical potentials*. At this point, we probably realize how we can understand thermal dynamical processes: they are the result of the *difference between hot and cold*.

1.1.2 System Dynamics Models

The descriptions of the phenomena discussed above contain the seeds of formal explanations of physical processes. Take the case of communicating tanks in Fig. 1.1. A word model of the system and its processes might go like this. There is a pressure difference of the oil across the connecting pipe. As a result, oil will flow through the pipe from the point of higher to the point of lower pressure. By resisting the flow, the pipe regulates the current. This makes the volume of oil decrease in the first container, and increase in the second. Since the quantity of oil in a container sets up the pressure due to the action of gravity, the pressure difference between the tanks will go down, which will make the current of oil through the pipe decrease, and this will make the levels of oil in the tanks change more slowly, and so on.

Graphical modeling tools. There are system dynamics modeling tools that support us in translating these words into diagrams and equations. Liquid flowing from tank 1 to tank 2 diminishes the volume of liquid in tank 1 and increases it in tank 2. This basic idea is expressed graphically with storage and flow symbols (Fig. 1.5) whose combination represents *laws of balance*. The stored liquid sets up a pressure which depends upon the quantity of fluid and the size of the tank which is symbolized by a *capacitance*: The greater the volume the higher the pressure, with the capacitance as the factor relating one to the other. The flow, finally, depends upon the pressure difference and a material factor that tells us how hard it is for the fluid to flow (this factor is called flow *resistance*).

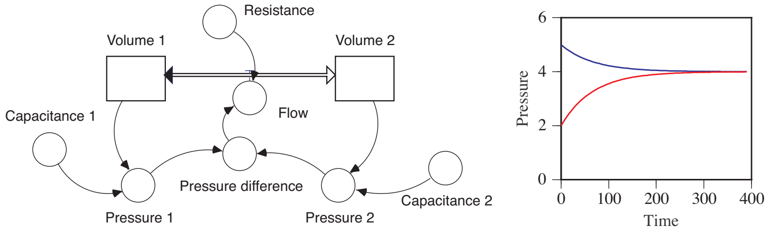

Figure 1.5: A system dynamics model diagram (left, produced with the program Stella, isee systems 1986-2010) and its simulation. Rectangles represent stored quantities, fat arrows symbolize transports, and circles stand for further variables and parameters that are connected by thin arrows. The model equations are shown further below.

The structure of the model has now been represented graphically. We still need to cast our ideas into formal expressions. The software used to draw the diagram lets us enter the relevant relations in mathematical form. Here is a concrete example:

$$\text{d (Volume\_1) / dt} = -\,\text{Flow} \;,\quad \text{Volume\_1(0)} = 10$$
$$\text{d (Volume\_2) / dt} = \text{Flow} \;,\quad \text{Volume\_2(0)} = 2$$

$$\text{Pressure\_difference} = \text{Pressure\_2} - \text{Pressure\_1}$$

Flow = – Pressure_difference/Resistance
Pressure_1 = Volume_1/Capacitance_1
Pressure_2 = Volume_2/Capacitance_2

Resistance = 100
Capacitance_1 = 2
Capacitance_2 = 1

In this example. values and units are arbitrary. Numerical software solves this set of equations leading to pressures (and volumes and flow) as functions of time as shown in the graph of Fig. 1.5. Quite obviously, the numerical result shows the same behavior as experimental values obtained in the example of Fig. 1.1. In practice, we use data to determine parameters of the model such as the flow resistance: parameter values are changed and the simulations are fitted to experimental values. In the example discussed here, the ideas built into the model give close to perfect agreement between model and reality. Therefore, we accept the assumptions that (a) the pressure of oil in a tank is proportional to its volume, and (b) the flow of oil through the pipe is proportional to the driving force (pressure difference).

Extending and changing models. Extending and changing the model produced above becomes quite intuitive and simple when we use the graphical modeling tools available to us today. Imagine that one of the tanks in Fig. 1.1 had an additional outlet, or we used water instead of oil. In the first instance, we would simply add a flow element to one of the tanks in the model diagram of Fig. 1.5 and express the flow in terms of the appropriate pressure difference and a resistance. In the second case, we would have to change the form of the relation between pressure differences and flows (it would no longer be linear).

Analogical reasoning. The model constructed for this first example can be transferred to electrical systems (Fig. 1.6). Take the example of driving electric charge from one capacitor to another with the help of a battery (or power supply), as in Fig. 1.4. You can use the system dynamics model constructed for communicating tanks (Fig. 1.5, left), change the names of the variables (replace volume by charge, pressure by potential or voltage), and add the effect of the power supply by specifying a fixed value of a driving potential difference which is added to the potential difference between the capacitors, and the model is completed. Equations for potentials and for the flow do not have to be changed. The correspondence between fluid and electric dynamical phenomena will become even more evident in an example from physiology discussed in some detail below.

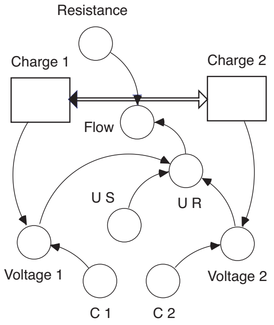

Figure 1.6: Diagram of a system dynamics model for a circuit containing two capacitors, a resistor, and a power supply (U_S stands for the voltage of the power supply).

Structure of dynamical models. The model—represented by the equations listed above—has a structure worth noting. There are two *laws of balance* of volume of oil including two *initial values* (the volumes at the beginning of the process). We observe that the flow leaving the first tank must be equal to the flow entering the second storage element. This is a special case of the balance of volume which we might call the *interaction rule*. A *relation between pressure differences* in a circuit tells us how to relate the pressure difference across the pipe to those across the fluid columns in the tanks. Then there are three *constitutive relations* for pressures of stored fluids and for the flow, and three *parameters*. The laws of balance and the relation between pressure differences have a generic structure that is the same in all systems. The constitutive laws, on the other hand, depend upon circumstances. To be specific, if we had let water flow through the pipe, the flow law would be different from what we used for oil.

1.2 A Complex Case: The Blood Circulatory System

The concepts and methods used in Section 1.1 for creating an understanding of dynamical systems are basic, yet they suffice for some fairly sophisticated models of real complex cases. This will be demonstrated by constructing models of the blood circulatory system. At the same time we will see how analogical reasoning is employed in an active field of research and development. Researchers in physiology use the language of electric circuits to describe their models of the blood circulatory system.

1.2.1 Description of the System

Historically, it was not self evident that one could understand the blood circulatory system in terms of hydraulics. Today, we are accustomed to seeing the heart as a pump and the vessels as pipes for the flow of blood. Briefly said, the circulatory system consists of a single circuit having two pumps made up by the two main chambers (ventricles) of the heart (Fig. 1.7).

The blood circulatory system. The right ventricle of the heart pumps blood through the lungs (through the *pulmonary circuit*) where it is replenished with oxygen. From there it flows to the left side of the heart into the atrium and then into the main chamber called the *left ventricle*. From there the blood is pumped through vessels through the body. The "pipe" leading away from the heart is called the *aorta* which branches off into arteries, which branch into finer vessels and capillaries. There are several branches of this body circuit (called the *systemic circuit*) going through the torso with its organs, through the legs and arms, and through the head. After the blood has brought oxygen, nutrients, and water to body parts and has taken up waste products, it flows back through the veins toward the right ventricle of the heart. If we want to understand blood pressure properly, we need to understand how the aorta functions.

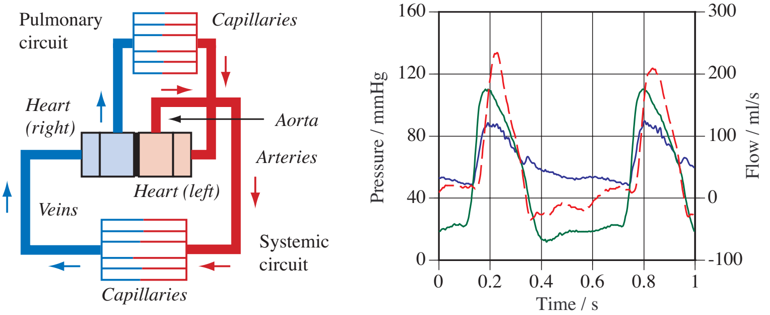

Figure 1.7: Left: Schema of our cardiovascular system. Right: Blood pressure and blood flow measured in a sheep, as functions of time. The solid pressure curve that changes from about 110 mmHg to less than 20 mmHg was taken inside the left ventricle. The second pressure curve (solid line, with values between 50 and 90 mmHg) was measured in the aorta near the heart. The flow in the aorta near the heart is shown as the dashed line (with values on the right vertical axis).

Blood pressure. We have probably all had our blood pressure measured at one time or another. An air filled cuff is put around our upper arm. The pressure of the air is increased until the cuff fits tightly. Then the pressure is slowly decreased and the doctor listens for changes of sound and then reports something like "130 over 80." The upper value is called the *systolic pressure*, the lower one is the *diastolic pressure* (Fig. 1.7).

First, we have to remember that the values reported are typically given in units of mmHg (millimeters of mercury column, i.e., the pressure that supports a column measuring so many mm of mercury; 1 bar correspond to about 760 mmHg). Second, a value of zero means “ambient” pressure, i.e., the average pressure in the body which is close to ambient air pressure.

Why are there two values reported in blood pressure measurements? Why isn’t the lower value simply zero or close to zero, considering that the pressure in the left ventricle reaches a value close to zero at some point during the cardiac cycle? The aorta and its properties are responsible for this. The aorta is a flexible vessel, in contrast to arteries and capillaries. This means that the aorta functions not only as a pipe but also as a storage vessel—very much like a balloon or a membrane accumulator. It stores the blood that comes from the left ventricle for some time and releases it relatively steadily into the rest of the circuit, i.e., into the arteries and capillaries. These basically work as simple pipes that let the blood pass. Their hydraulic function is described by stating that they set up a resistance to the flow of the relatively viscous blood. The blood pressure measured at the doctor’s office is close to the pressure measured in the aorta. This quantity varies rhythmically between a high value (somewhat lower than the maximum pressure in the heart) and a lower one. Since there always is blood in the aorta, this lower (systolic) value is never close to zero (Fig. 1.7).

1.2.2 An Electric Circuit Modeling the Action of the Aorta

In summary, the left ventricle is the intermittent pump for the systemic circuit, the aorta is like a windkessel,[2] and the rest of the blood vessels serve as a (branching) pipe (see Fig. 1.8, top left). Between the pump and the windkessel there is the aortic valve which must make sure that blood does not flow back into the left ventricle. Such a system can be modeled successfully by a physical model using electric elements—power supply, capacitors, resistors, and a diode (Fig. 1.8, bottom left). Operating the circuit with a variable voltage of the power supply that mimics the pressure of blood in the left ventricle leads to a voltage across the capacitor analogous to the blood pressure in the aorta (see the graph on the right in Fig. 1.8).

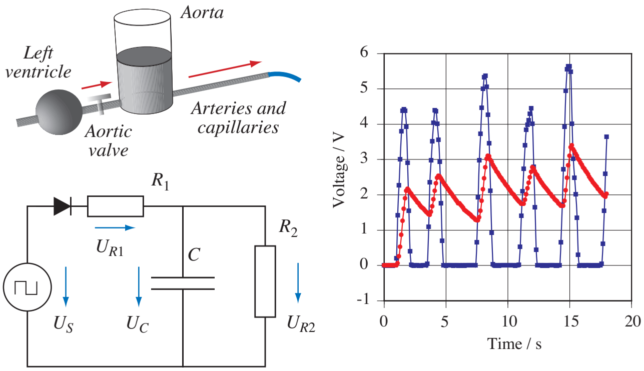

Figure 1.8: The windkessel model of the systemic circuit (top left). It consists of a pump that takes liquid from the environment (left), a short pipe with a valve, a container, and a (long) pipe leading back to the environment. Analogous electric circuit (bottom left) having a power supply, diode, resistors, and a capacitor modeling the aorta. Operating the electric circuit with a variable voltage of the power supply leads to data shown on the right.

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[2] Around 1660, windkessel pumps were invented to smooth water flows through fire hoses. Without these, the flows directed at a fire would be as intermittent as the pressure differences set up by hand operated pumps used in old fire fighting systems. (Windkessel is German for air or wind chamber.)

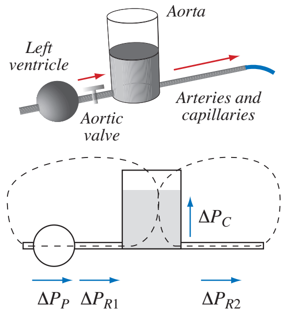


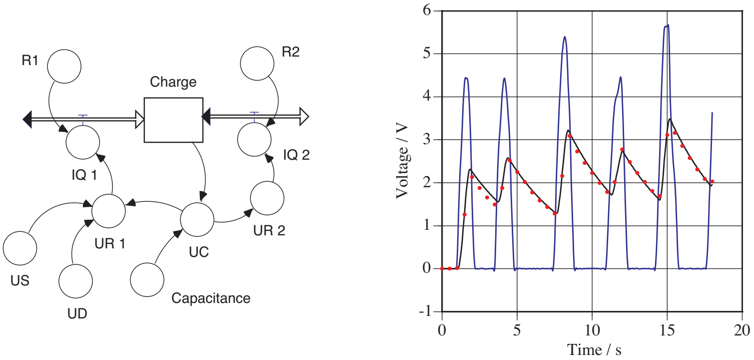
Figure 1.9: The windkessel system features two independent loops. Along a loop, the sum of all pressure differences is equal to zero.

To produce the equivalent electric circuit for the hydraulic windkessel, it is important to identify voltages with pressure differences and to make sure that the relation between potential differences in a circuit (i.e., the loop rule) is adhered to. Here, we have two loops, one leading from the ambient air through the pump and the valve to the tank and back to the environment, the second leading from the environment through the tank and the long pipe back to the ambient air (Fig. 1.9). The intermittently driven pump is represented by a power supply that sets up a voltage as a function of time resembling the pressure difference of the pump.

System dynamics model. Creating a system dynamics model of the electric circuit—and by analogy for the heart-aorta-vessels part of the systemic blood flow system—is rather simple (Fig. 1.10, left). The fit of simulations and data can be made close to perfect for the electric circuit (Fig. 1.10, right) whereas the model will always be too simple to represent the physiological system very well. Still, it gives us a clear understanding of important processes in the blood flow system.

There is a single law of balance of electric charge of the capacitor (analogous to volume; see the reservoir symbol in the system dynamics diagram of Fig. 1.10). Charge can flow through two resistive elements (pipes), one associated with the circuit through the power supply (pump), the other going through the second resistive element (long pipe). If we use the ideas applied before, the flows through the resistive elements are expressed in terms of the voltages (pressure differences) across them, and the respective resistances. The voltage across the capacitor (pressure of the fluid in the tank) is calculated with the help of the charge and the capacitance. The valve is imitated by a diode. Finally, the resistive voltages are calculated from the other voltages using the loop rule.

Figure 1.10: Diagram of system dynamics model of electric windkessel (left). Data and simulation results are on the right. The dots are from the experimental data of UC, whereas the solid line closely following the dots is the simulation result. The source voltage (US) is used as input to the model.



The model equations consist of a law of balance, two loop rules relating voltages, and five constitutive relations for the resistors, the diode, the capacitor, and the power supply:

$$d\,(\mathrm{Charge})\,/\,dt = IQ\_1 - IQ\_2 \;, \quad \mathrm{Charge}(0) = 0$$

$$UR\_1 = US - UD - UC$$

$$UR\_2 = UC$$

$$IQ\_1 = \mathrm{IF}\ (UR\_1 > 0)\ \mathrm{THEN}\ UR\_1/R1\ \mathrm{ELSE}\ 0$$

$$IQ\_2 = UR\_2/R2$$

UC = Charge/Capacitance
US = Graphical_Function(TIME)
UD = 0.82

Capacitance = 458e-6
R1 = 1.00e3
R2 = 1.0e4

1.2.3 Limitations of the Model

The model for the electric circuit representing the windkessel system is quite good. The only real shortcoming is the strongly simplified model of the diode. Here, we assume the diode to be ideal: it does not let any charge pass for voltages across the element that are smaller than 0.82 V; above that, it is an ideal conductor. This is a crude approximation of the real behavior, but apparently it suffices.

If we transfer the model to the physiological case (by simply changing names of variables and parameters, and by applying proper values for the hydraulic parameters), limitations become more apparent. Experience with such models shows that the expressions for the capacitive pressure of the blood in the aorta, and for the flow through the aortic valve, could be improved upon. The aorta is a pressure vessel having an elastic wall which typically leads to a nonlinear relation between pressure and volume stored. The flow from the left ventricle into the aorta is quite complex (narrowing of the conduit, a valve, relatively high flow speed) so that the flow relation turns out to be nonlinear as well. Using a relation for turbulent flow instead of laminar flow comes closer to reality.

Another shortcoming is demonstrated by the shape of the simulated aortic pressure. With a pressure of the blood in the left ventricle taken from measurements (see the diagram in Fig. 1.7), the simulated pressure curve looks more like that in Fig. 1.10. There is no hump near the maximum values, with a slower decrease after the closing of the aortic valve. We do get this behavior, however, if we apply a more realistic representation of the aorta in our model. Rather than taking the aorta as a single piece (with the blood having a single value of the pressure), we divide the vessel into several elements. The dynamics of the fluid is represented by storage in each element and flow from element to element (as in Fig. 1.1 and Fig. 1.5). This pseudo-finite-element model yields results that are better already.

Finally, there is one more important limitation in all of the models produced so far. If we limit our concepts to those of storage and flow through resistive elements, we will never understand why blood flows backward for a brief period during the cardiac cycle (see the flow data in the diagram of Fig. 1.7). Note that this does not mean that blood flows back through the valve into the heart of the animal. Rather, the liquid flows back and forth in the aorta, mostly forward, but backward as well. We will discuss how to understand this later in this chapter (Section 1.6).

The limitations discussed have to do with the constitutive laws for storage and flow applied in our models. The generic laws of balance of amounts of liquid or electric charge, and the concept of pressure differences and voltages in circuits are unaffected, and so is the basic assumption that fluid and electric phenomena can be described by similar basic structures in dynamical models. We will see in this book how we can apply this type of analogical reasoning to construct a theory of the dynamics of heat.

1.3 WATER, CHARGE, AND DRIVING FORCES

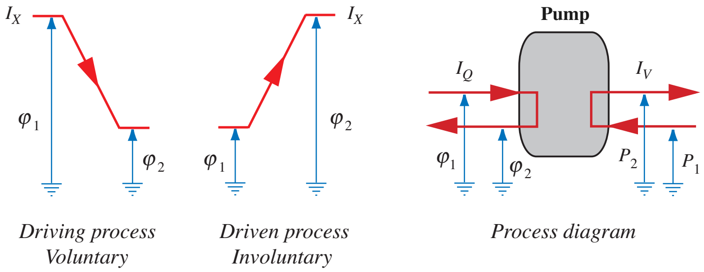
We have been fairly successful in producing practical models without much regard for formalisms. In the present and the following sections, I will present a more formal discussion of what we can learn from dynamical fluid and electric systems and the modeling exercises just described. I will introduce the basic quantities needed to formulate ideas, and discuss the most important relations between these quantities that make up our models of dynamical systems.

1.3.1 Basic Explanatory Schemas and Physical Quantities

Let us review the structure of explanations used in our models of fluid and electric dynamical systems discussed so far. A process is visualized as the result of the *storage and flow of fluidlike quantities* such as amount of fluid or electric charge. A flow going through a *potential difference*—pressure difference or electric potential difference—from high to low is said to run by itself. Potentials are visualized as *levels*, and a potential difference is conceptualized as a *driving force*. Flows can be forced through a potential difference going in the opposite direction—up instead of down—by a pump. Finally, flows through conduits are resisted, and if a fluidlike quantity is stored, it literally sets up a tension (a potential difference) in the system.^{3}

The interaction of fluidlike quantities and differences of levels is the source of dynamics in the world. If differences decay, we end up in equilibrium where processes stop; if the processes build up new differences, dynamics continues in waves through chains of systems. The schemas listed here (substances, intensities, driving forces, resistances, tensions) are aspects of a gestalt of natural processes constructed by human perception. They form the basis of our understanding of nature.

Waterfalls and process diagrams. The relationship between fluidlike quantities and their associated driving forces (potential differences) can be cast in graphical form. In a *voluntary process*, a fluidlike quantity flows from a higher to a lower level of the potential—like water in a waterfall (Fig. 1.11, left). The reverse is a fluidlike quantity being forced through a potential difference from a low to a high level, like water being pumped uphill. This I call an *involuntary process* (Fig. 1.11, center).



Driving process
Voluntary

Driven process
Involuntary

Process diagram

Figure 1.11: Both water and electrical charge (X) may be imagined to flow by themselves from regions of higher potentials (φ) to regions of lower ones. Potentials are conceptualized as levels. I_X is the flow of quantity X. Coupling of processes is represented in process diagrams (right; this is a diagram for an ideal water pump). I_Q and I_V represent flows of charge and of volume, respectively. P stands for pressure.

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[3] What is still missing from this description is an explicit reference to the force or power of a process which can be take as the source of our concept of energy (see Chapter 2).

Physical systems often couple processes where a voluntary process drives an involuntary one (Fig. 1.11, right). An example of this is an electrically driven water pump. Here, electric charge flowing downhill drives the flow of water from low to high pressure. The diagram used to represent the coupling of phenomena is called a *process diagram*.

Fundamental or primitive quantities. Our first question must be which physical quantities we can use as the basis for a quantitative description of the flow and storage of fluids and electric charge. From the foregoing discussion of explanatory schemas it should be clear that we need to formalize the concepts of *amounts of fluidlike quantities*, their *flows*, and associated *levels* of fluids or electricity.

There is an important difference between fluidlike quantities and intensities which helps us in keeping them apart. The former scale with the size of a system whereas the latter do not. Take a body carrying electric charge and divide it into two equal parts. Half of the body carries half of the charge. The electric potential, however, is the same for both parts of the body (if it were not, charge would flow and rearrange upon bringing the two parts of the body together again). The difference between the two types of quantities is reflected in the terms *extensive* or *additive* for amounts of fluid or charge, and *intensive* for pressure and electric potentials.

Measures of amounts. To be concrete, let us consider water in a container. There are several possible choices for measures of its amount, namely, *volume* of a certain amount of the liquid, its *mass* or *amount of substance* (Chapter 6). These measures are related:

$$\begin{aligned} m &= \rho V \\ n &= \frac{1}{M_0} m \end{aligned} \tag{1.1}$$

V, m, and n stand for volume, mass, and amount of substance, respectively. The conversion factors are the density ρ and the molar mass M_0. Standard SI units of volume, mass, and amount of substance are m^3, kg, and mole. We shall express most of what follows in terms of the volume of a body of water. Using the volume of an amount of fluid is the basis of descriptions of hydraulic processes. Amount of substance will become important when we turn to a chemically oriented discussion of transport processes. Mass is sometimes preferred in mechanical engineering models.

The physical quantity which measures an amount of electricity is well known: it is the *electric charge*. A capacitor stores a certain amount of charge, just as a container stores a certain volume of water. In contrast to quantities of fluids, quantities of charge can take positive and negative values.

Measures of flows. If we want to set up a theory of the flow and balance of water and charge, we need a primitive quantity which describes their transport. For this purpose we conceive of the *rate of flow of water or charge into or out of a system*, measured in terms of a new quantity which we call the *flux*[4] or the *current* of water or charge

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[4] We often find the term flux associated with what we will call flux density, namely the rate of flow divided by the surface area through which the current is flowing. Here, we follow the tradition of electromagnetism, where we speak of electric or magnetic fluxes as the surface integrals of the flux densities, which are the quantities **E** or **B**.

(informally, I will use the term *flow*). The rate at which water flows can be expressed in terms of the *volume flux* or *current of volume*, i.e., the volume of water flowing past a measuring device per time. Its unit is m^3/s. Alternatively, we may employ the flux of mass or the flux of amount of substance. Again, for practical purposes, we shall choose the first of these measures for simple fluid processes. In electricity, the quantity analogous to volume flux is the *current of charge* whose unit is Ampere (A).

We shall use the symbol I for fluxes or currents. Since there will be many fluxes for different physical phenomena, indices will be used to distinguish between them. Here, the index V stands for volume, Q for charge. So I_V and I_Q stand for currents of volume and charge, respectively.

Measures of levels. Using volume and volume current, we are able to say something about an amount of water, namely the amount of it stored in a system, and the rate at which it is flowing. These quantities do not suffice for a complete theory of the phenomena associated with containers of water and currents flowing in and out. They do not tell us anything about why water should be flowing at all. In electrical circuits as well, we need a quantity which is responsible for setting up currents of charge in the first place. As we have already discussed, we introduce *potentials* or, figuratively speaking, *levels* to make sense of this aspect of our conceptualization of reality. In fluids, *pressure* takes this role; in electricity, it is the *electric potential*. Pressure is measured in Pascal (Pa), electric potential in Volt (V).

Derived quantities. Only hindsight can tell us if we have chosen the right quantities as the fundamental ones for a given range of phenomena. This means that we have to accept a certain choice, define new quantities on its basis, build a theory, and work out its consequences. If we are satisfied with the results compared to what nature demonstrates, we call the theory a successful one.

For the following, let us define derived quantities related to volume and volume current. Again, the case of electricity is analogous. An important derived quantity for the description of dynamical phenomena is the *rate of change* of stored quantities of fluid (volume) or charge; it measures *how fast* quantities change. The *rate of change of volume* is visualized as the slope of the graphical representation of the function $V(t)$ or, more precisely, the slope of a tangent to the function at a chosen point of time (Fig. 1.12). Symbols for rates of change of volume are dV/dt or the letter V with a dot on top (read as V-dot).

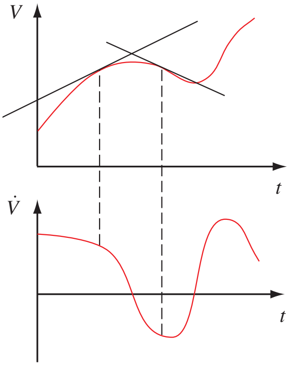

Figure 1.12: Determining the rate of change of volume by calculating the slope of tangents to the $V(t)$ curve. The symbol V with the dot above it denotes the rate of change of V.

$$\dot{V} \equiv \frac{dV}{dt} \tag{1.2}$$

Often we are interested in the overall change of the volume of water in a container as the result of a process lasting for a period of time. For this purpose we define the *change of volume* which is simply given by

$$\Delta V(t_1 \to t_2) = V(t_2) - V(t_1) \tag{1.3}$$

The change of volume is related to the rate of change. It is the integral over time of the rate of change of volume:

$$\Delta V = \int_{t_1}^{t_2} \dot{V} dt \tag{1.4}$$

Finally, we need a measure of how much water has flowed across a surface with a current in a given period. We shall call this quantity the *volume exchanged* or *volume transported*. It is defined as the integral over time of the flux of volume:

$$V_e = \int_{t_1}^{t_2} I_V \, dt \tag{1.5}$$

As mentioned, analogous expressions hold for quantities relating to electric charge.

1.3.2 Accounting for Volume and Charge

Fluidlike quantities such as volume, amount of substance, or electric charge accumulate in systems, and there is a simple law of accounting for such quantities called a *law of balance*. Consider water. If the volume of water is a conserved quantity (as should be the case for incompressible fluids not subject to chemical conversions) the volume stored in a given system can change only due to the transport of water across the surface of the system (Fig. 1.13). There must be currents or fluxes of volume with respect to the system, and they alone are responsible for the change of the contents of the system. They determine how fast the volume changes:

> *The rate of change of the volume of water in the system must be equal to the sum of all fluxes associated with the currents of water crossing the surface:*

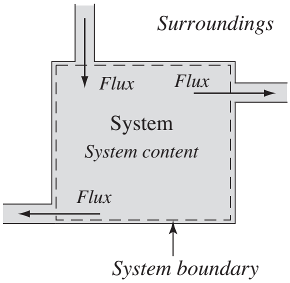

Figure 1.13: A system is a region of space occupied by a physical object. It is separated from the surroundings by its surface. A fluidlike quantity which we imagine to be stored in the system can change as a consequence of transports across its boundary. Currents leaving a system are given negative fluxes. In some cases, transport across the surface is the only means of changing the contents.

$$\frac{dV}{dt} = I_{V,net} \tag{1.6}$$

This is taken as one of the most fundamental relations of a theory of dynamics. Here, $I_{V,net}$ is the *sum of all currents* with respect to the system chosen (Fig. 1.13). Note that the quantity we call *flux* has the dimensions of the quantity which is flowing divided by time. If we write the law of balance in this form, we have implicitly assumed that the flux of a quantity flowing *into* a system should be given a *positive* sign.

Equ.(1.6) is *not* a definition of the currents or fluxes of volume. The quantities occurring in this equation are fundamentally different, related only by an interesting property of fluidlike quantities. If we could no longer assume the volume of water to be a conserved quantity, we would have to change the law of balance. We would be forced to account for other means of changing the volume, by introducing other terms in Equ.(1.6). For now, let us assume that this is not necessary.

The definitions of change and of transported quantities (Equations (1.4) and (1.5)) allow us to express the law of balance of volume in the following form:

$$\Delta V = V_{e,net} \tag{1.7}$$

I call Equ.(1.6) the dynamical or *instantaneous form* of the law of balance of volume, whereas Equ.(1.7) is the *integrated form*. Identifying processes with flows, and expressing laws of balance, is the first important step in systems analysis.

In the case of electricity, the laws and definitions are identical. Since charge is a strictly conserved quantity, the rate of change of the charge of a body must be equal to the sum of all currents of charge with respect to this body. In other words, the law of balance of electric charge looks exactly like Equ.(1.6), with volume replaced by charge:

$$\frac{dQ}{dt} = I_{Q,net} \tag{1.8}$$

The change of charge and the amount of charge exchanged in a process are defined analogously to Equations (1.4) and (1.5). Again, the law of balance in integrated form looks just like the expression in Equ.(1.7).

There is a special expression of the instantaneous law of balance of charge that is often used in modeling of electric circuits. Consider a junction of three or more wires in a composite circuit. Charge flowing toward the junction from one or more wires then leaves directly through the other wires. This is so because the junction does not store charge. The charge of the junction is and remains equal to zero. Therefore, the rate of change of charge of the junction must be zero as well, which means that for a junction,

$$0 = I_{Q1} + I_{Q2} + \ldots \tag{1.9}$$

This is called the junction rule or Kirchhoff's First Law. Clearly, the same relation must hold for the balance of volume of a liquid applied to a junction made of pipes.

1.3.3 Pressure Differences and Voltages

Pressure differences and voltages are considered causes for processes. Alternatively, we may look at processes leading to potential differences. Identifying such differences and related processes is the second integral part of systems analysis.

Pressure differences in circuits. The pressure of a fluid changes from point to point in a closed hydraulic circuit. To make use of this observation, choose a few important points in the system (usually at the inlets and outlets of elements such as pipes, pumps, and tanks). Label *pressure differences*[5] from point to point (Fig. 1.14) by introducing arrows and symbols ΔP_{AB}, etc.:

$$\Delta P_{\text{AB}} = P_{\text{B}} - P_{\text{A}} \tag{1.10}$$

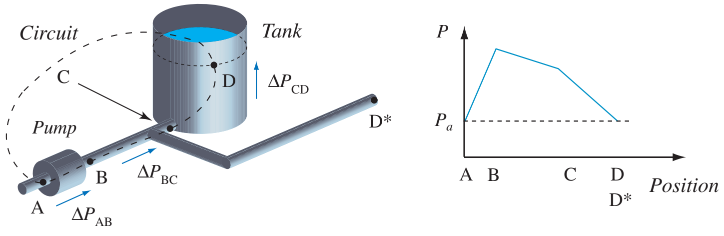

Figure 1.14: Pressures in a fluid system (left) form a kind of "pressure landscape" or "hydraulic landscape" which shows ups and downs (right, level diagram).

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[5] Note that there are two different kinds of (mathematical) differences in nature. One refers to a change in time as in Equ.(1.3). Then there are also differences of a quantity associated with their change along a path as in Equ.(1.10). I typically call the former *change* and the latter *difference*.

We can draw a diagram looking like a “landscape” (Fig. 1.14). When we are back at the origin, the pressure is the same. Therefore, the sum of all pressure differences in a closed circuit must be equal to zero (loop rule, Kirchhoff’s Second Law):

$$\Delta P_{AB} + \Delta P_{BC} + \Delta P_{CD} + \ldots = 0 \tag{1.11}$$

Electric potential and voltages. The electric potential measures the intensity of the electric state of a system at a point (these systems can be material bodies such as wire, but also electric fields). Its unit is V (Volt), the symbol used is φ or φ_{el}. Electric potential does not have an absolute zero point (in contrast to pressure). This means that only the differences of electric potentials are important.

Electric potential differences are called *voltages* (see below). By itself, positive electric charge will flow from points of high to low electric potential, whereas electrons flow from lower toward higher electric potentials. The potential difference is the difference of potentials at two different points A and B of a system (Fig. 1.15), independent of the physical reasons for the difference:

$$\Delta\varphi_{AB} = \varphi_B - \varphi_A \tag{1.12}$$

The *negative* potential difference is called the *voltage* between points A and B:

$$U_{AB} = -\Delta\varphi_{AB} \tag{1.13}$$

This means that the voltage is positive across a resistor in the direction of the flow of (positive) charge, whereas it is negative across a battery in the direction of flow.

Potential differences (voltages) in closed electric circuits. The potential changes from point to point in a closed electric circuit. To make use of this observation, choose a few important points in the system such as the circuit of Fig. 1.15. Label potential differences (voltages) from point to point by arrows and by symbols U_{AB}, etc.

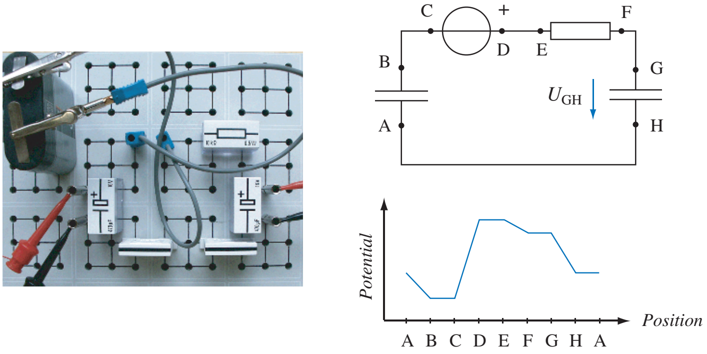

Figure 1.15: Electric potential as a function of position in a circuit containing two capacitors, a battery, and a resistor. The values will change in the course of time, but the form of the level diagram will basically remain the same.

We can draw a diagram looking like a “landscape” (Fig. 1.15). When we are back at the origin, the potential is the same. Therefore, the sum of all voltages in a closed circuit must be equal to zero (loop rule, Kirchhoff’s Second Law):

$$U_{AB} + U_{BC} + U_{CD} + \ldots = 0 \tag{1.14}$$

1.4 SOME CONSTITUTIVE RELATIONS IN FLUIDS AND ELECTRICITY

The relations discussed in Section 1.3 are basic or generic: they take the same general form in different systems and processes. Laws of balance and relations between level differences along a path in a system are independent of special circumstances. This is not so for the relations between potential differences, stored quantities, and currents. The latter depend upon special circumstances—upon how a system is built, the materials used, etc. For this reason we call the relations needed to express the terms in laws of balance *special*, *material*, or *constitutive laws*.

1.4.1 Resistive Transports of Fluids and Charge

When a fluid flows through a pipe, its pressure drops in the direction of flow because of fluid friction. This pressure drop is called a *resistive pressure difference* ΔP_R, and it is characteristic of the flow which, in turn, depends upon fluid properties and pipe dimensions. Charge flows through a resistor (or a conductor) from higher to lower electric potentials, so there is a resistive voltage U_R associated with this process.

Process diagram of resistive transports. Since a fluid goes from high to low pressure (different from what it does in a pump), or charge flows from high to low electric potentials, we say that the level differences are driving the process. We know that in resistive transports, the process caused by the flow of fluid or charge consists of the production of heat (Fig. 1.16).

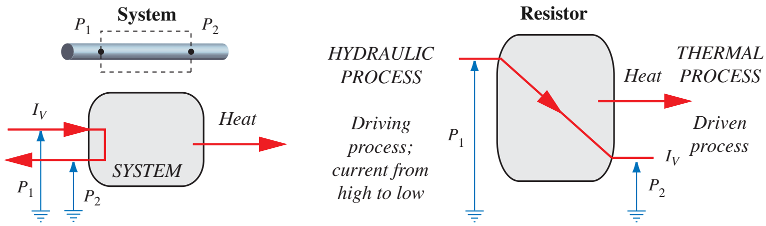

Figure 1.16: Process diagram of resistive fluid flow. The flow element may be called a resistor. Here, the driving process is the flow of fluid. The driven process consists of the production of heat. Right: Waterfall representation of the driving process. The case of electricity is analogous.

Flow characteristic for fluids. The relation between the resistive pressure drop ΔP_R and the associated volume current is called the *flow characteristic* (Fig. 1.17). (Note that here the current I_V measures the flow *through* the system.) It allows us to calculate flows if we know the associated pressure difference, or vice-versa. There are two types of flow (laminar and turbulent) leading to two different characteristic curves.

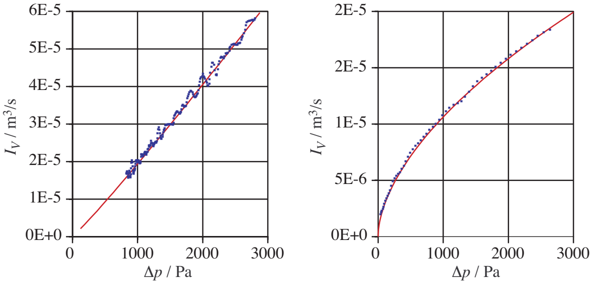

Figure 1.17: Flow characteristics for laminar flow (oil in a pipe, left) and for turbulent flow (water in a pipe, right). I_V is the symbol for volume current.

Analogous characteristic relations can be constructed for electric conductors. The simplest conductors are made of ohmic materials where the relation between resistive voltage and electric currents is linear as in the case of laminar flow (Fig. 1.17, left). When we let electricity pass through a wire that can change its temperature drastically—as in the filament of an incandescent light bulb—characteristic curves look more like those on the right in Fig. 1.17 (even though the material is still ohmic; the deviation from linearity is not due to a basic change in transport mechanism, but to increasing temperature). A completely different type of transport of charge is observed in diodes which are made of combinations of semiconductors. Here, the electric current grows exponentially with increasing voltage across the diode.

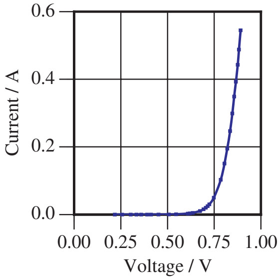

Figure 1.18: Characteristic diagram of a diode.

Laminar Flow. For laminar flow, the characteristic relation is linear. In this case, we can write the flow law with the help of a *hydraulic conductance* G_V (units m^3/(s·Pa)) or its inverse, the *hydraulic resistance* R_V (units Pa·s/m^3):

$$I_V = -G_V \Delta P_R \quad \text{or} \quad I_V = -\frac{1}{R_V}\Delta P_R \tag{1.15}$$

There is an expression for the hydraulic conductance or resistance for laminar flow in pipes with circular cross section which is called the law of Hagen and Poiseuille:

$$R_V = \frac{8\mu l}{\pi r^4} \tag{1.16}$$

r and l are the radius and length of the pipe, μ is the viscosity of the fluid. The viscosity of a fluid tells us how “thick” it is.[6] Viscosity is discussed in some more detail in Chapter 3.

Turbulent flow. In turbulent flow, the flow increases less rapidly with an increase of the associated pressure difference (diagram on the right of Fig. 1.17). The turbulent characteristic function is close to the square root function for many practical cases:

$$I_V = k\sqrt{|\Delta P_R|} \tag{1.17}$$

This simple relation suffices as a first approximation. k is called the *turbulent flow factor*. This factor is similar to a conductance, however, the terms resistance and conductance are only used for laminar flow.

Ohmic transport of charge. The transport of charge in metallic conductors satisfies a simple relation. For small enough voltages or electric currents, the current is strictly proportional to the potential difference across the conductor. Therefore, the characteristic relation is linear. In this case, we can write the flow law with the help of a *conductance G* (units A/V = 1/Ohm) or its inverse, the *resistance R* (V/A = Ohm = Ω):

$$I_Q = GU_R \quad \text{or} \quad I_Q = \frac{1}{R}U_R \tag{1.18}$$

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[6] For a derivation of the law of Hagen and Poiseuille, and for a comparison of conductive transports of momentum, heat, and mass, see Bird, Stewart, and Lightfoot (1960) or any other book on transport phenomena.

There is an expression for the conductance or resistance for ohmic transport in conductors having constant cross section:

$$R = \rho_{el} \frac{l}{A} \tag{1.19}$$

l and A are the length and cross section of the conductor, respectively, and ρ_{el} is the *resistivity* of the material. The resistivity basically measures how hard it is for charge to flow through the conductor. The inverse of resistivity is called *electrical conductivity*: $\sigma = 1/\rho_{\mathrm{el}}$ (unit: S/m, S: siemens).

1.4.2 Storage of Fluids and Charge

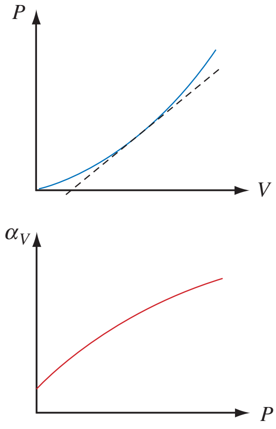

Figure 1.19: Pressure as a function of stored volume (top). The slope of the characteristic curve is called the elastance of the storage element. Typically, the elastance is a function of pressure. The case shown here is characteristic of the fluid in the human eye.

Constitutive laws specifying currents have to do with transport phenomena. We also need a means of saying something about the process of storing water (or electrical charge). It is customary to introduce a quantity which expresses the relationship between a change of the amount of fluid contained in a system and the change of the associated potential, i.e., the change of pressure. It allows us to relate the change of system content to the possibly more easily measured potential. In electricity we are interested in the relationship between the charge contained in a system and the voltage.

Capacitive characteristic in fluid systems. If fluids are stored in tanks or pressure vessels, the pressure difference (normally) increases with an increasing amount of stored fluid. In other words, there is a relation between the volume stored and the associated pressure difference (which we call a *capacitive pressure difference* ΔP_C). The relation is called a *capacitive characteristic* (Fig. 1.19).

Elastance and hydraulic capacitance. The characteristic can be expressed mathematically if we introduce the *elastance* α_V, i.e., the factor which tells us how easy it is to increase the pressure with a given amount of fluid:

$$\begin{aligned} \dot{P}_C &= \alpha_V \dot{V} \\ \Delta P_C &= \alpha_V \Delta V \quad \text{if} \quad \alpha_V = const. \end{aligned} \tag{1.20}$$

α_V is equal to the slope of a tangent to the characteristic curve (Fig. 1.19). This means that the elastance measures the stiffness of container walls (in the case of pressure vessels) or the inverse of the cross section of a tank. The unit of elastance is Pa/m^3. Alternatively, we can introduce the *hydraulic capacitance* C_V (units m^3/Pa) which is defined as the inverse of the elastance ($C_V = 1/\alpha_V$):

$$\begin{aligned} \dot{V} &= C_V \dot{P}_C \\ \Delta V &= C_V \Delta P_C \quad \text{if} \quad C_V = const. \end{aligned} \tag{1.21}$$

For a liquid of density ρ in an open container the capacitance is

$$C_V = A(h)/(\rho g) \tag{1.22}$$

Equ.(1.21) suggests a way to determine volume changes from pressure changes if the capacitance is known (as a function of pressure). For constant capacitance, we simply multiply the pressure difference by the capacitance. Geometrically, this corresponds to the calculation of the area of a rectangle. This tells us that, in general, the change of volume associated with a change of pressure is equal to the area between the capacitance – pressure function and the pressure axis (Fig. 1.20).

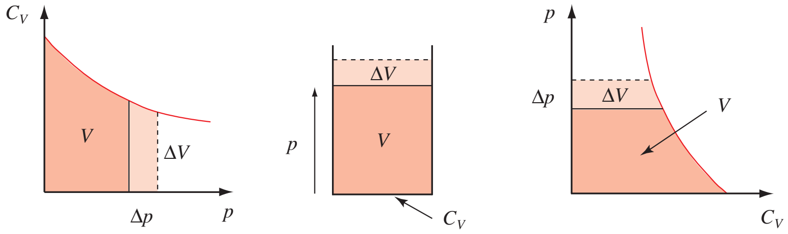

Figure 1.20: The change of volume related to a change of pressure is obtained from integrating the capacitance over pressure (left). This can be interpreted more intuitively by considering the diagram as a type of tank with a fluid contained in it (center and right).

Electric capacitive characteristic. If charge is stored in a capacitor, the voltage increases with increasing amount of stored charge. In other words, there is a relation between the charge stored and the associated voltage (which we call a capacitive voltage U_C). The relation is called a *capacitive characteristic* (Fig. 1.21, left). Another way of representing the relation is by drawing a fluid image (Fig. 1.21, right), an imaginary tank with charge inside where the level represents the voltage U_C. In general, the characteristic is nonlinear. A linear characteristic is related to a constant capacitance. The cross section of the imaginary tank represents the capacitance of the capacitor.

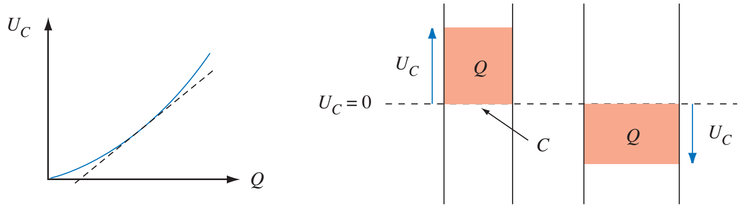

Figure 1.21: Voltage as a function of stored charge (left). The slope of the characteristic curve is called the elastance of the capacitor. Fluid image of capacitors (right). A capacitor is like a tank storing charge (Q) which can be positive or negative. The level in the "tank" depends upon the quantity stored through the cross section of the tank. Here, the cross section symbolizes the capacitance.

Elastance and capacitance. The characteristic relation can be expressed mathematically if we introduce the *elastance* α_Q, i.e., the factor which tells us how easy it is to increase the voltage with a given amount of charge:

$$\begin{aligned} \dot{U}_C &= \alpha_Q \dot{Q} \\ U_C &= \alpha_Q Q \quad \text{if} \quad \alpha_Q = const. \end{aligned} \tag{1.23}$$

α_Q is equal to the slope of a tangent to the characteristic curve (Fig. 1.21). This means that the elastance measures the "stiffness" of the storage system. The unit of elastance is V/C.

Alternatively, we can introduce the electric capacitance C_Q or simply C (units C/V = F (Farad)) which is defined as the inverse of the elastance ($C = 1/\alpha_Q$):

$$\begin{aligned} \dot{Q} &= C_Q \dot{U}_C \\ Q &= C_Q U_C \quad \text{if} \quad C_Q = const. \end{aligned} \tag{1.24}$$

1.4.3 Pumps and Batteries

Pumps, batteries, generators, and solar cells drive fluid or electric processes, i.e., they set up pressure differences and voltages. The driving process can be electric or mechanical in the case of pumps. Batteries are driven chemically, generators mechanically, and solar cells get their input from solar radiation.

Process diagram and characteristic of pumps. Pumps come in many different types and forms, ranging from the heart to microengineered or large industrial pumps. Here we are only interested in their overall performance. Pumps make fluids flow, and they increase their pressure. This simple fact is best represented in a process diagram of the type shown in Fig. 1.22. The process diagram used to describe the operation of a pump can be used to introduce the notion of the energy delivered to the fluid by the pump (Chapter 2).

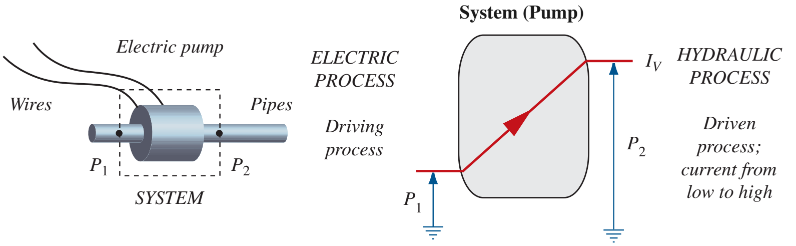

Figure 1.22: As a fluid is forced through a pump, its pressure is made to go up. Figuratively speaking, the fluid current is forced uphill.

We define the operation of a pump by describing the relation between the pressure difference ΔP_P set up and the flow through the device. An ideal pump might be described by assuming a constant pressure difference. Real pumps commonly have a more complicated type of characteristic (Fig. 1.23). If we model a real water pump as consisting of an ideal part that sets up a pressure difference, followed by a resistive element due to turbulent flow, we should get a parabolic pressure-flow relation (this corresponds well to what we see in the diagram on the left of Fig. 1.23).

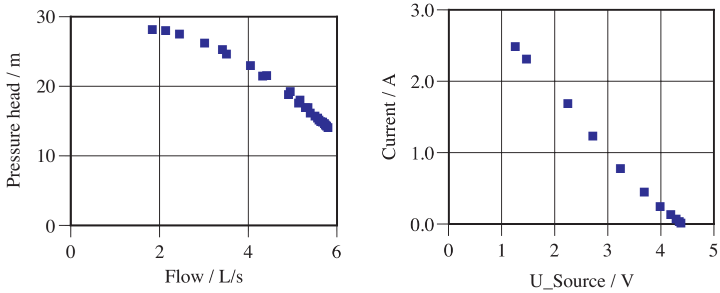

Figure 1.23: Measured characteristic curves of a water pump (left) and a typical 4.5 V battery. Whereas the water pump pumps water, a battery pumps electric charge.

Characteristics of batteries. Characteristic diagrams of batteries are simple linear curves: The voltage across the terminals decreases with increasing electric current (see Fig. 1.23, right). The formal description of the characteristic is

$$U_B = U_0 - R_i I_Q \tag{1.25}$$

U_B is the voltage measured across the terminals, U_0 is the maximum possible voltage (the *open circuit voltage*), I_Q is the current through the battery, and R_i is the internal resistance of the battery. A derivation of Equ.(1.25) uses ohm's relation for resistive transports of charge.

1.4.4 Gravity and Height Differences

In the case of fluids, gravity—the Earth's gravitational field—plays an important role if we do not restrict our view to purely horizontal processes. The action of gravity leads to particular constitutive relations for fluids in tanks and (vertical) pipes.

Hydrostatic pressure. For fluids which are "stacked" in a gravitational field, i.e., systems where the weight of the fluid is responsible for a pressure difference, there is a simple relation between pressure difference and height difference (Fig. 1.24). It can be derived from the observations which are summarized in Fig. 1.25:

$$\Delta P_{Grav} = -\rho g\left(h_{\mathrm{B}} - h_{\mathrm{A}}\right) \tag{1.26}$$

This relation can be used to calculate pressure differences (and capacitive characteristics) for fluid tanks (Fig. 1.20 and Equ.(1.22)). It is correct for constant density only.

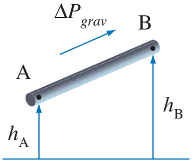

Figure 1.24: Going uphill in a fluid "stacked" in the gravitational field, the pressure decreases.

Pressure gradients. According to the example of hydrostatic pressure in an incompressible liquid (Equ.(1.26)), the pressure gradient in the upward direction is

$$\frac{dP}{dh} = -\rho g \tag{1.27}$$

As observed in Fig. 1.25, the pressure gradient is proportional to the density of the liquid. Furthermore, it must depend upon the *strength of gravity* (g). The negative sign tells us that the pressure decreases if we go upward.

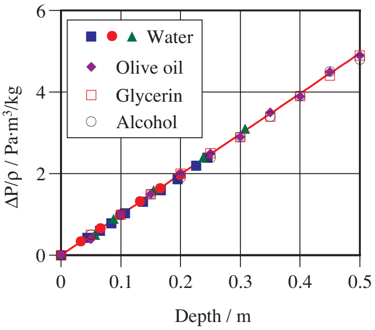

Figure 1.25: Pressure increases downward in a liquid at a fixed "rate" (gradient). The gradient depends upon density ρ and gravity g.

Pressure in the Earth's atmosphere. The pressure-height relation for the atmosphere is not linear: the pressure of the air drops exponentially with height above ground. This is so since the fluid is a gas whose density changes with pressure (and temperature). Nevertheless, the expression for the vertical pressure gradient is the same as that for incompressible fluids, i.e., Equ.(1.27) still holds.

If we know how the density of the air depends upon pressure and temperature, the relation for hydrostatic equilibrium (Equ.(1.26)) can be solved. Even though this is not realistic, one often considers the case of an *isothermal* atmosphere (an atmosphere where the temperature does not change in the vertical direction). If this is the case, the density is proportional to the pressure (see Problem 7 in Chapter 5) leading to an exponential pressure-height relation:

$$P(h) = P(0)e^{-h/k} \tag{1.28}$$

For the Earth's atmosphere, the factor k is about 7000 m. This means that the pressure decreases by a factor of e for every 7000 m, or by a factor of 2 for every 5000 m. Even though our atmosphere is not isothermal, the result is useful for quick estimates.

The gravitational potential. Pressure differences are interpreted as hydraulic driving forces, pressures are hydraulic "levels." For fluids stacked in the gravitational field, vertical pressure differences are the result of gravity. They are calculated according to Equ.(1.26) or Equ.(1.27). If we multiply the pressure difference by the volume of a certain quantity of liquid which we imagine to be transported from a height h_1 to a height h_2 (Fig. 1.26), we have $\Delta PV = \rho g \Delta h V = g \Delta h \rho V = g \Delta h m$:

$$\Delta PV = -(g\,\Delta h)m \tag{1.29}$$

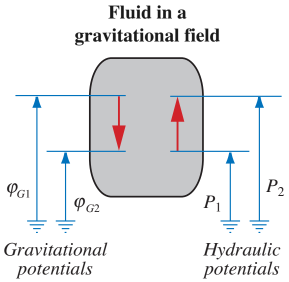

Figure 1.26: A process diagram explaining the coupling of gravitational and hydraulic processes. As a body of mass m goes "downhill by a distance" $g\Delta h$, the pressure of the corresponding volume goes up by ΔP.

This result is interpreted as follows (Fig. 1.26). If we look at gravitational processes as the transfer of the mass of a substance from a level 1 to a level 2, the right hand side of Equ.(1.29) represents mass m going from a gravitational level gh_1 to a level gh_2. Therefore, $g\Delta h$ is interpreted as the *gravitational driving force*, and gh is the so-called gravitational potential.

1.5 BEHAVIOR OF *RC* MODELS

The models we can construct by using laws of balance, loop rules, and resistive and capacitive constitutive relations are called *RC* models. *R* and *C* stand for resistance and capacitance, respectively. Adding pumps and batteries does not change anything about the nature of the models we have been building. As we will see, the behavior of such models is relatively simple. In particular, they do *not* admit oscillatory solutions. We will see in the following section how to extend models to create an understanding of oscillatory behavior and wave motion.

1.5.1 Charging and Discharging Single Storage Elements

Systems made up of containers and pipes (or capacitors and resistors) show relatively simple behavior. Complex behavior is often the result of the interaction of several simple elements. For the simplest systems—those having constant values of capacitance and resistance—analytic solutions of the model equations can be obtained. Solutions are combinations of exponential functions of time. In the case of draining straight-walled tanks through horizontal pipes with laminar flow (Fig. 1.27, top) we get

$$\Delta P(t) = \Delta P_0 e^{-\frac{t}{R_V C_V}} \tag{1.30}$$

If an empty tank is charged (Fig. 1.27, bottom), the solution of the model is

$$\Delta P(t) = \Delta P_{Max}\left(1 - \exp\left(-\frac{t}{R_V C_V}\right)\right) \tag{1.31}$$

Equ.(1.30) and Equ.(1.31) also hold for $h(t)$ and $V(t)$, and they work for the equivalent electric circuits. We only have to substitute electric for hydraulic variables.

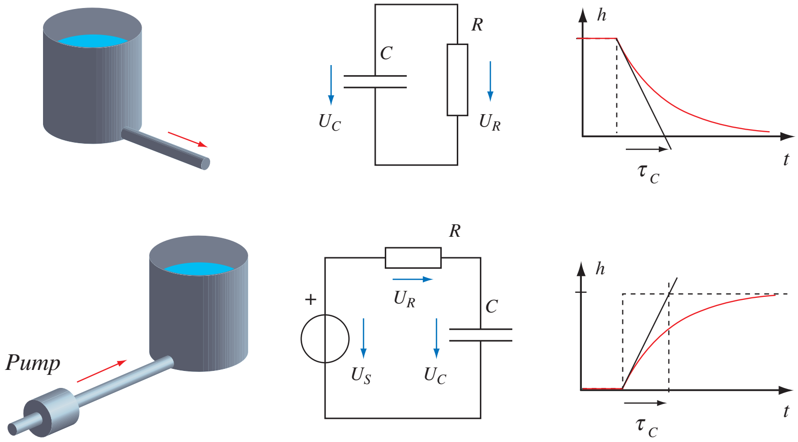

Figure 1.27: Draining or filling of straight walled tanks through pipes showing laminar flow leads to exponentially changing functions. The initial rate of change is used to define the time constant τ_C of the system (Section 1.5.2). Analogous electrical circuits (shown in the middle) show the same behavior.

The functions reported above are the solutions of the differential equations resulting from the combination of all the relevant model equations. Here is an example of the draining of the oil tank. We have a single storage element with a single flow. Therefore, the law of balance of volume is

$$\frac{dV}{dt} = I_V$$

The volume is related to the capacitive pressure difference, the flow results from the resistive pressure difference along the pipe, and the pressure differences are equal:

$$\begin{aligned} V &= C_V \Delta P_C \\ I_V &= -\frac{1}{R_V}\Delta P_R \\ \Delta P_C &= \Delta P_R \end{aligned}$$

If we introduce these equations into the law of balance of volume, we obtain a single differential equation:

$$C_V \frac{d\Delta P_C}{dt} = -\frac{1}{R_V}\Delta P_C$$

An initial condition has to be added to this differential equation: $\Delta P_C(0) = \rho g h_0$. Solving the initial value problem leads to a function of the type seen in Equ.(1.30).

1.5.2 Time Constants

The behavior (fluid level as a function of time) for the simple cases of draining and filling of a tanks is shown in the accompanying graphs (Fig. 1.27). The solutions of the model are exponential functions. A measure of how fast (or slow) the process is, is the time it would take for the tank to drain or to fill were the level to continue to change at the initial rate. This time span is called the *capacitive time constant* τ_C of the system. In a period equal to one time constant, the level of fluid in the system shown on the left in Fig. 1.27 drops to $1/e = 0.37$ times the initial level. The analytic solutions in Equ.(1.30) and Equ.(1.31) demonstrate that

$$\tau_C = R_V C_V \tag{1.32}$$

1.5.3 Conductive Transports Through Chains of *RC* Elements

If we combine storage elements and resistors (or conductors) in long chains (see Fig. 1.28), we obtain models of a phenomenon that is very common in natural and technical settings: *diffusion*. Diffusion is usually associated with the transport of substances through matter. An everyday example is the spreading of a drop of ink on blotting paper, or salt dissolved in a layer of water slowly migrating into other parts. Diffusion is particularly important in biology where many processes depend on the transport of chemicals through bodies (see Chapter 6 for more detail).

Diffusion is very much a physical process. As we have seen, fluidlike quantities such as charge or amount of substance can be transported (later we will add heat and momentum to the list). One form of transport is the flow through conducting materials. A fluidlike quantity is present in matter (it is stored), and it is conducted through it (Fig. 1.28). The combination of effects leads to diffusion.

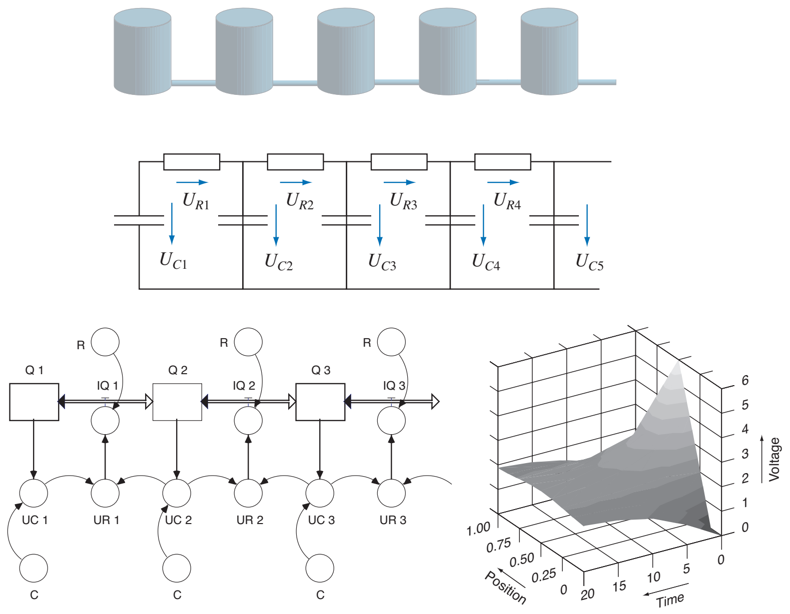

Figure 1.28: A chain of tanks connected by pipes (top) stores and conducts a fluid. The resulting behavior is found in diffusion. The same phenomena are observed in chains of electric *RC* elements (middle: the equivalent circuit for the row of tanks). Bottom left: A system dynamics model diagram for the electric *RC* system. Bottom right: Simulation result for the SD model. Here, we assume a circuit analogous to a row of tanks without an outflow to the environment. Charge placed near the middle of the *RC* line spreads like a substance in diffusion through matter until the electric potential has become the same everywhere.

Consider several tanks in a row connected by pipes as in Fig. 1.28. This is the simplest and most vivid of systems whose behavior mimics diffusion. The tanks are for temporary storage of a fluid, and the pipes let the fluid pass according to the law of conduction (or resistance): The flow depends upon the difference of fluid levels in the storage elements. Alternatively, we can build an equivalent electric circuit that demonstrates analogous behavior (Fig. 1.28, middle). This is a model of a thin electric conductor such as a wire. It can be considered to consist of storage elements for charge placed one after another along a line. The wire also acts as the conductor. If we place some charge near the middle of such a conductor, electricity will spread toward the ends as shown in the diagram of Fig. 1.28 (bottom, right).

1.6 OSCILLATORY PROCESSES AND WAVES

We still do not understand an important element of the behavior of dynamical systems. I have pointed this out when we discussed the blood flow system (Section 1.2.2). Blood flows backward in the aorta for brief periods during each cardiac cycle—the flow oscillates back and forth. The windkessel model in the form presented in Fig. 1.10, however, does not lead to oscillations.

This shortcoming is no problem for the example of how oil flows from one tank into another through a pipe. However, if we change the system to a U-pipe containing a less viscous liquid (Fig. 1.29), oscillations occur. So we need to understand what we have neglected in our discussions so far.

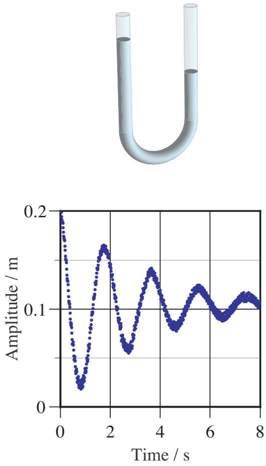

Figure 1.29: Many systems exhibit oscillatory behavior. Here we have mercury in a U-pipe.

1.6.1 Starting and Stopping Currents

Contrary to what we would consider realistic, we have assumed that currents follow pressure differences directly and in accordance with a simple flow relation such as the ones in Equ.(1.15) and Equ.(1.17) (and Equ.(1.18) for electricity). To be concrete, the model of the equilibration of levels in two communicating tanks (Fig. 1.5) predicts an immediate rise of the current from zero to its maximum value upon opening the valve of the connecting pipe (Fig. 1.30).

This is unrealistic. We know from experience that a current of water starting in a pipe takes a noticeable amount of time to reach its maximum. The same is true of electric currents, even though the delay there may be so much shorter that we think we can neglect the effect in all our models. This is not so, however. The phenomenon of *induction*, as it is called in electricity, is present all the time, and it can be made very noticeable by introducing electromagnets in the form of solenoids in our circuits.

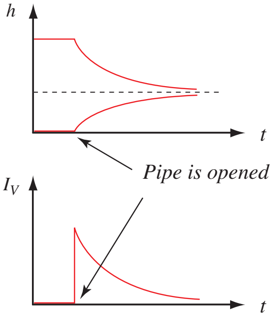

Figure 1.30: As the pipe connecting two fluid tanks is opened, the current of fluid suddenly jumps to its initial value.

Both in fluids and in electricity, currents have to be driven to start up, or put more generally, to change. Driving means we need a pressure difference or a voltage for the effect to occur. The beginning phase of draining of a tank through a pipe (Fig. 1.31) demonstrates how we can understand this phenomenon. As we open the pipe (take the finger off the end of the pipe) to let the fluid flow, a pressure difference is established along the pipe. (Even though this process also takes some time, we shall assume, and reasonably so, that this happens quickly compared to the rise of the current we are interested in.) This pressure difference results from the difference of pressures at the inlet of the pipe at the tank and the pressure of the air at the outlet. It will slowly decrease in time due to the draining of the tank. (This is the phenomenon we already understand on the basis of our *RC* models.)

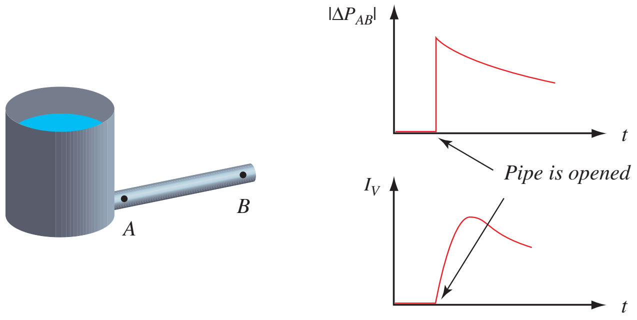

Figure 1.31: A fluid discharging through a long horizontal pipe. The current cannot jump suddenly to the value calculated according to the resistance law. Rather, it rises gradually.

What we need to understand is this: there is a real pressure difference ΔP_{AB} along the fluid in the pipe. At the very beginning, when the flow is still zero, the resistive pressure difference which we have been considering so far in this chapter must also be zero. So, there is an actual pressure difference that has nothing to do with the actual flow. Rather, the pressure difference leads to an acceleration of the fluid: the fluid in the tank presses more strongly upon the fluid in the pipe from behind than does the air at the outlet from the front. Now, as the current of fluid increases, the resistive pressure difference associated with it increases as well. As a result, the part of the actual pressure difference ΔP_{AB} remaining, i.e., the quantity $\Delta P_{\mathrm{AB}} - \Delta P_R$, also decreases. This is the part that continues to accelerate the fluid. The flow will increase more slowly as time goes on, just as indicated in the lower diagram of Fig. 1.31. Finally, the inductive effect—the changing of the current due to the driving force $\Delta P_{\mathrm{AB}} - \Delta P_R$—must have come to a halt.

The pressure difference $\Delta P_{\mathrm{AB}} - \Delta P_R$ is called the *inductive pressure difference* ΔP_L:

$$\Delta P_{\mathrm{AB}} = \Delta P_R + \Delta P_L \tag{1.33}$$

Hydraulic induction results from the inertia of the fluid flowing through a pipe (electric induction is caused by the magnetic field of a solenoid)[7]. Therefore, its should be possible to derive the relation between rates of change of currents and inductive pressure differences on the basis of the laws of mechanics. Newton's law (i.e., the balance of momentum; see Chapter 3) lets us calculate the accelerating effect of the inductive pressure difference:

$$-A_p \Delta P_L = A_p l \rho \frac{dv}{dt}$$

where A_p is the cross section of the pipe, and l is its length. We assume the flow speed to be uniform over the entire cross section of the pipe. Therefore, the pressure difference may be expressed in terms of the rate of change of the volume flux (or volume current):

---

[7] While energy is stored in the magnetic field associated with a current of charge, energy is stored in the flowing water (kinetic energy). The form of the relationship between energy, current, and inductance is the same in hydraulics and electricity (see Chapter 2).

$$\Delta P_L = -\frac{l\rho}{A_p}\frac{dI_V}{dt}$$

The factor $l\rho/A_p$ is called the hydraulic *inductance* of the fluid in the pipe (in analogy to the electromagnetic inductance of a solenoid in electric circuits):

$$L_V = \frac{l\rho}{A_p} \tag{1.34}$$

This factor measures how hard it is to change a current. Now we can write the law of induction, i.e., the relation that shows in what way an inductive pressure difference leads to a rate of change of a current:

$$\Delta P_L = -L_V \frac{dI_V}{dt} \tag{1.35}$$

In electricity, we have an analogous relation:

$$\Delta\varphi_{el,L} = -L\frac{dI_Q}{dt} \tag{1.36}$$

Note that these equations are constitutive laws, not some sort of law of balance of a current. Hydraulic and electric phenomena are clearly comparable. As in the case of electric currents, decreasing a current of water induces a positive potential difference which tends to oppose the change of volume flux.

If we want to know how a laminar fluid current through a pipe (or, in analogy, an electric current through a solenoid having ohmic resistive properties) changes in time, we simply combine Equ.(1.33) and Equ.(1.35) to obtain

$$\Delta P_{\text{AB}} = -R_V I_V - L_V \frac{dI_V}{dt} \tag{1.37}$$

I have written the relation for the hydraulic case, but you may translate it to fit electric phenomena by simply substituting charge for volume. The ratio of inductance and resistance has the dimension of time. Therefore, *L/R* is the characteristic time scale on which currents change in an inductive circuit (the *inductive time constant*). If we assume a constant value for the total pressure difference, the solution of Equ.(1.37) for the starting of a current is an exponential of the type shown in the lower diagram of Fig. 1.27. The formal solution proves that *L/R* is the inductive time constant.

1.6.2 Oscillations

The explanation of the phenomena associated with starting and stopping of currents is the missing link for an understanding of oscillatory systems. If we combine electric or hydraulic capacitors and inductors, oscillations are possible. In an electromagnetic *LCR*-circuit, charge oscillates between storage and flow with a frequency which depends mainly on *L* and *C*. Water may be made to oscillate in a U-tube in just the same manner (Fig. 1.29). By calculating the capacitance and the inductance of the container we can find the frequency of oscillation. There is another hydraulic setup which has an electronic equivalent. If the flow of water from an artificial lake to the turbines of an electric power plant has to be stopped abruptly for any reason the pressure may rise to such a level that the pipes rupture. For this reason a hydraulic capacitor is built in parallel to the system, namely a tower (surge tank) which is filled rapidly with the water rushing down the pipes.

Let me derive the equations of a simple oscillator by creating a system dynamics model for a fluid in a U-pipe (Fig. 1.29). The U-pipe is structurally similar to two communicating tanks described in Fig. 1.1. So let us start with the system dynamics model presented in Fig. 1.5. The relations it represents are still valid. Only the flow relation has to be turned around: since the current will be calculated by integrating its rate of change (which we obtain from the law of induction), we can use the flow to compute the resistive pressure difference (Fig. 1.32). The difference of the capacitive pressures yields the total pressure difference along the pipe (ΔP_p). The latter minus the resistive pressure difference yields the inductive pressure difference ΔP_L. This is used to calculate the rate of change of the current. This completes the system dynamics model shown in Fig. 1.32. Here, *C* is the capacitance of one of the sides of the pipe, *L* is the inductance of the fluid in the pipe, and *R* is its resistance. Properties are assumed to be constant.

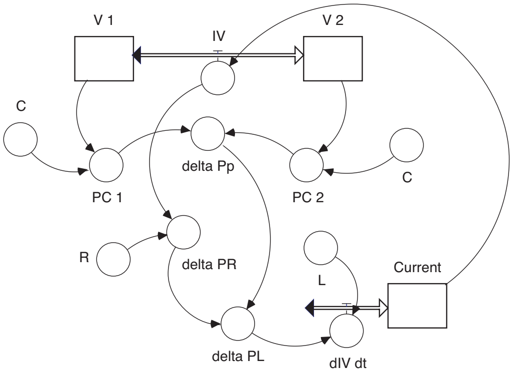

Figure 1.32: A system dynamics model diagram for a fluid in a U-tube. Note the integrator for the current (the combination of flow symbol for the rate of change of the current and the stock for the current itself). The inductive pressure difference is calculated from the capacitive and resistive pressure differences.

The equations that make up the model are three differential equations (one for each of the stocks), the loop rule, and constitutive relations for the rate of change of the current, the capacitive pressures, and the resistive relation. These equations can be rearranged to yield two initial value problems (first order ordinary differential equations with initial conditions). If we express these equations with two of the three state variables, namely P_{C1} and I_V, we obtain

$$\begin{aligned} \frac{dP_{C1}}{dt} &= -\frac{1}{C} I_V \ , & P_{C1}(0) &= P_{C1,0} \\ \frac{dI_V}{dt} &= -\frac{1}{L}\left(-2P_{C1} + RI_V\right) \ , & I_V(0) &= I_{V,0} \end{aligned} \tag{1.38}$$

It is customary to combine such equations still further so we have a single second order differential equation for one of the variables. If we choose P_{C1}, we arrive at

$$\frac{d^2P_{C1}}{dt^2} + \frac{R}{L}\frac{dP_{C1}}{dt} + \frac{1}{LC_{tot}}P_{C1} = 0 \tag{1.39}$$

with proper initial values for P_{C1} and dP_{C1}/dt. This is the well known linear equation for damped oscillations. If $R = 0$, the oscillation is undamped, and its period is

$$T = 2\pi\sqrt{LC_{tot}} \tag{1.40}$$

Note that the total capacitance, i.e., the capacitance of both sides of the U-pipe taken together, is equal to half the capacitance of one side, so $C_{tot} = C/2$.

1.6.3 Inductive Model for Blood Flow

Notice how induction leads to an explanation of the back-flow of blood in the aorta of a mammal (Fig. 1.7). Assume the aorta to be a storage element (it has flexible walls), a resistor or conductor (it lets viscous blood pass), and an inductor (the fluid demonstrates inertia). A simple model of the dynamic behavior of the aorta is one that divides the vessel into two sections (Fig. 1.33). The storage elements and the flow between them can now be modeled like a system made up of a fluid in a U-tube (Fig. 1.32). The difference is that we have an input to and an output from the U-tube (intermittent input from the heart, smoothed output to the body).

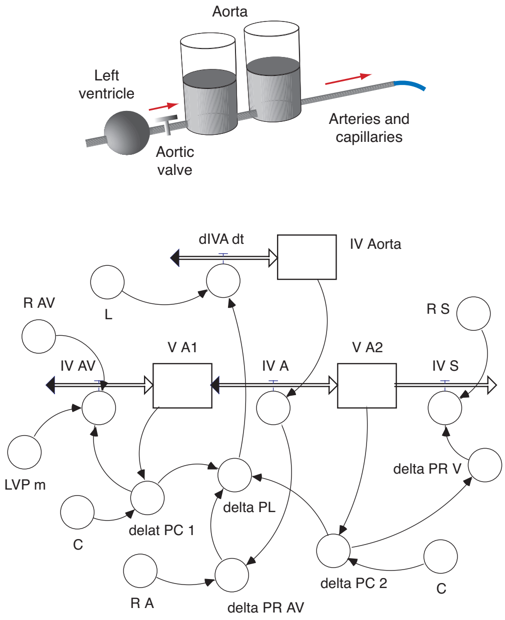

Figure 1.33: If we divide the aorta in the blood circulatory system into two elements, the windkessel model looks like the illustration at the top. The flow between the two tanks can be made to exhibit both resistive and inductive properties. Bottom: A system dynamics model diagram of this system.

The model contains quite a number of parameters which have to be determined if we want reasonable simulation results. It is important to have data to estimate at least some of these values (see the graph in Fig. 1.7). The aortic pressure curve and the flow allow us to estimate the capacitance of the aorta and the systemic resistance (we obtain values of $2\cdot10^{-9}$ m^3/Pa for the former, and $2\cdot10^8$ Pa·s/m^3 for the latter). The difference between the pressures in the left ventricle and the aorta yields an estimate of the resistance of valve and entrance to the aorta (or, if we model the flow there as turbulent, the flow factor as in Equ.(1.17); we obtain roughly $4\cdot10^{-6}$ m^3/(s·Pa$^{0.5}$)).

We still need starting values for the inductance and resistance of the aorta. If we assume a hose of 50 cm length and 1 cm diameter for the aorta of a sheep, the inductance should be about $6\cdot10^6$ Pa·s^2/m^3 (Equ.(1.34)). For laminar flow, the resistance would be roughly $7\cdot10^6$ Pa·s/m^3 (Equ.(1.16)). If we use the inductance and the capacitance of the aorta to estimate the period of oscillation of blood in this vessel as in Equ.(1.40), we obtain 0.35 s. This can be compared to the oscillations visible in the flow data. Armed with such values, we can simulate the model in Fig. 1.33, and adjust parameters a little more. despite this overly simplified model, we obtain results that do mimic many of the important real features (Fig. 1.34).

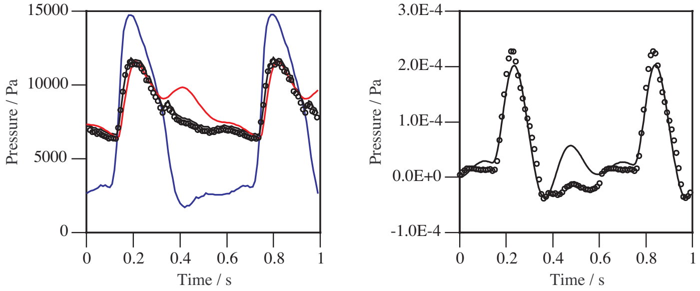

Figure 1.34: Data for blood pressure (left) and blood flow (right) in the aorta of a sheep (circles in the diagrams; see also Fig. 1.7). Simulation results for the model in Fig. 1.33 have been superimposed. The results are far from perfect, but they show behavior not visible in *RC* models discussed earlier. There are wave-like features both in the pressure and in the flow.

1.6.4 Wave Propagation in Chains of *LCR* Elements

The inductive two-tank windkessel model is a step toward an explanation of another important phenomenon—*wave propagation*. If we divide a conductor into many elements and model each element as a storage device with a resistor and an inductor between each of them (Fig. 1.35), electric charge or a fluid will be transported in a wavelike manner through the chain. Whereas in *RC* chains (Fig. 1.28), a substance diffuses and basically does not flow backwards, here the fluidlike quantity can be reflected at an end of the chain and come back, and the amplitude can become higher in an element further down the chain, something that does not happen in diffusion. Most importantly, one can identify a definite finite speed of wave propagation. This is noteworthy since the equations predict infinite speed for diffusion—something that is quite unrealistic and unphysical (see Chapter 13).

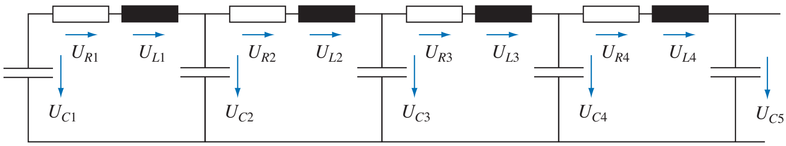

Figure 1.35: A chain of *RCL* elements can serve as a model for a conductor that admits wavelike transports. The black rectangles symbolize inductors.

A system dynamics representation of the chain of *RCL* elements in Fig. 1.35 is fairly simple to achieve. We start with the laws of balance of charge for two neighboring capacitors with a flow between them. This flow is calculated on the basis of the law of induction which necessitates knowledge of the inductive voltage U_L between the capacitors. This inductive voltage is a part of the total voltage between capacitors, i.e., $U_{C,i+1} - U_{C,i}$, if there is a resistive element. The part taken by the resistive element is calculated from $U_R = RI_Q$. Once we have a model for this part of the complete chain, elements can be copied and joined which leads to a model diagram such as the one shown in Fig. 1.36.

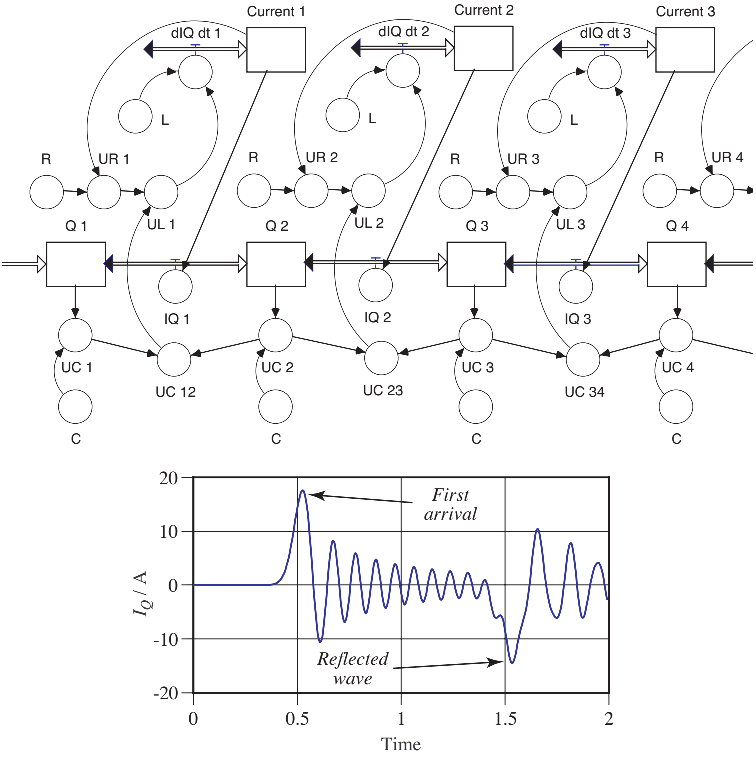

Figure 1.36: Top: Diagram of dynamical model of a chain of *LCR* elements as in Fig. 1.35. Bottom: Simulation of electric current at the center of a 1 m cable, represented by 40 *RCL* elements. Total capacitance: 1.0 F, total inductance: 1.0 H, resistance equal to zero. Input: A short pulse at $t = 0.025$ s. Note that it takes about 0.5 s for the input pulse to arrive at $x = 0.5$ m, and 1.5 s for the wave to reflect at the end of the cable and come back to the same point. This corresponds to a wave speed of 1.0 m/s.

Qualitative reasoning can give us an idea of which quantities the wave speed should depend upon (for a derivation of the wave equation and the speed of propagation see Section 3.6). Resistive properties of the chain lead to attenuation of the wave; they can be made smaller (even equal to zero, in theory) which lessens the damping but should not affect the wave otherwise. So we do not expect the resistance to determine the speed of propagation of a wave, at least not significantly. Inductance and capacitance, on the other hand, seem to be the factors that are directly responsible for wavelike behavior. We know that they determine the frequency of oscillation between two capacitors (Equ.(1.40)).

Take an electric coaxial cable and represent it in a simplified manner by an *RCL* chain as in Fig. 1.35. Assume that we have chosen 10 elements to model the cable. What keeps us from using 20 or 40 or still more element? Models with successively more elements should be better representations of the cable, not fundamentally different ones. Within limits set by how well a number of elements models the cable, each model should yield the same value for the propagation speed of the wave. Now, if we take 20 instead of 10 elements for the same physical object, we have to reduce the capacitances and inductances by a factor of 2. If we were to use a pair of values to calculate the wave speed, different models would lead to different results which contradicts our assumption. Therefore, it seems reasonable to assume that capacitance per length and inductance per length are the determining factors for wave speed:

$$c \sim \sqrt{\frac{l}{C}\frac{l}{L}} \tag{1.41}$$

c denotes the speed of propagation, and l stands for the length of the cable. The form is reasonable on grounds of physical units since the product of C and L has units of time squared. The product of capacitance and inductance per length has units of s^2/m^2, so Equ.(1.41) has correct units. Playing around with a dynamical model of a wave guide can confirm this hunch and tells us that the factor in Equ.(1.41) must be equal to one (see the simulation results in Fig. 1.36).

Both the models for diffusion in Fig. 1.28 and for wave propagation in Fig. 1.35 tell an important story for the later parts of this book. When we divide a body transporting a fluidlike quantity into ever smaller elements, we arrive at a model of spatially continuous processes. Waves will be taken up again briefly in Chapter 3, and continuous systems will be investigated in quite some detail in Parts III and IV of this book.

EXERCISES AND PROBLEMS

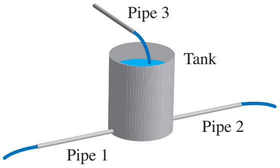

Figure P.2

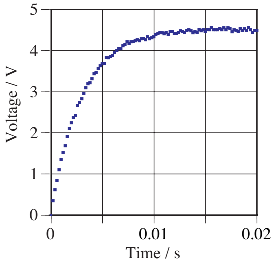

Figure P.3

1. Two currents of water are flowing into a fountain. The first changes linearly from 2.0 liters/s to 1.0 liters/s within the first 10 s. The second has a constant magnitude of 0.50 liters/s. In the time span from the beginning of the 4th second to the end of the 6th second, the volume of the water in the fountain decreases by 0.030 m^3. (a) Calculate the volume flux of the current leaving the fountain. (b) How much water will be in the fountain after 10 s, if the initial volume is equal to 200 liters?
2. Consider a tank having two outlets as in Fig. P.2. There is a *constant* inflow. Take vegetable oil as the liquid. Assume the tank to be half filled initially. How will the level of oil in the tank change in the course of time? Sketch a diagram showing different possibilities and explain how the different cases depend upon the magnitude of the inflow.
3. A battery is used to charge a capacitor through a resistor. The voltage across the capacitor has been measured as a function of time (Fig. P.3). The parameters of the system are to be determined with the help of a dynamical model. Resistance of the resistor, capacitance, internal resistance of the battery and open circuit (*oc*) voltage are unknown. (a) Sketch the diagram of a system dynamics model. (b) Formulate all equations of the model. (c) The open circuit voltage can be determined directly from the data. Why? How? Determine the *oc* voltage. (d) Determine the time constant of the circuit. (e) More experiments will be needed for a determination of all parameters. Describe possible measurements for a sufficient number of additional parameters. Show how the parameters can be determined. Assume that the elements of the circuit plus other similar elements are available for experimentation. Volt meters and ammeters and power supplies are available.
4. Derive the expression for the hydraulic capacitance of a U-pipe (as in Fig. 1.29). If you look at each of the sides of the U-pipe as a capacitor, are these capacitors connected in parallel or in series?
5. Two tanks (see Fig. P.5) contain oil with a density of 800 kg/m^3 and a viscosity of 0.20 $Pa \cdot s$. Initially, in the container having a cross section of 0.010 m^2, the fluid stands at a level

of 10 cm; in the second container (cross section 0.0025 m^2) the level is 60 cm. The hose connecting the tanks has a length of 1.0 m and a diameter of 1.0 cm. (a) What is the volume current right after the hose has been opened? (b) Calculate the pressure at A, B, C, and D at this point in time. The pressure of the air is equal to 1.0 bar, and C is in the middle of the hose. (c) Sketch the levels in the containers as a function of time. (d) Sketch an electric circuit which is equivalent to the system of containers and pipe. (e) Sketch a pressure profile (pressure as a function of position) for a path leading from A to D; include a point C* at the other end of the pipe from point B.

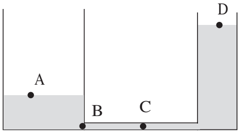

Figure P.5

6. A hydraulic windkessel system (Fig. P.6 left) consisting of an ideal pump, a valve and two identical containers is to be transformed into an electric system to be modeled formally (use and ideal diode for the valve). There is a short pipe between the containers. The diagram, Fig. P.6 right, shows the voltages across the (ideal) power supply (square wave signal) and across the two capacitors. Values of resistances and capacitances are assumed to be constant. The resistance of the resistor corresponding to the pipe leading to the environment is 1000 Ω.

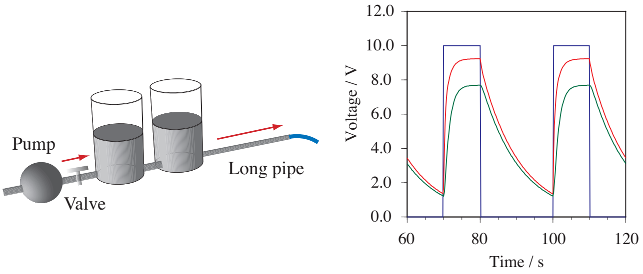

Figure P.6

(a) Sketch, label, and explain an electric circuit diagram that corresponds to the windkessel model. (b) Sketch the diagram of a system dynamics model for the electric windkessel circuit. Use electric symbols for quantities. (c) Formulate all relevant equations of the model. (d) Shortly after switching on the power supply, the capacitor voltages become constant (roughly between 75 s and 80 s). Why? Give a formal explanation. Use this to determine the missing resistances. (e) Use the behavior of the system to show that the capacitance of a single capacitor must be roughly equal to 5 mF. (f) What is the electric current between the capacitors shortly before 80 s?

7. The figure (Fig. P.7.1) shows an electric circuit. Resistances and capacitances are constant. The capacitance of the first capacitor is $C_1 = 1.0 \cdot 10^{-4}$ F. Create a hydraulic model for the circuit; perform the calculations for the electric quantities. Initially, the first capacitor is charged, the second one is uncharged. At $t = 0$ s, the first switch (S1) is closed, the second one stays open. The diagram, Fig. P.7.2, shows the voltage across the first capacitor.

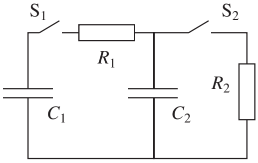

Figure P.7.1

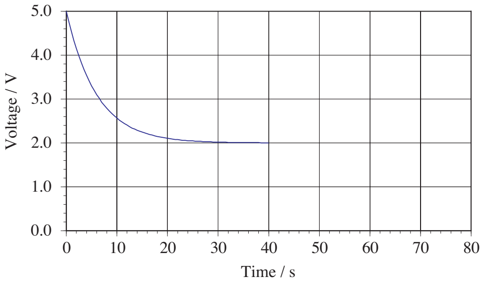

Figure P.7.2

(a) Sketch a hydraulic system that corresponds to the electric circuit (b) Sketch the diagram of a system dynamics model for the hydraulic system. (c) Formulate all the equations of the *hydraulic* model. (d) Sketch the voltage across the second capacitor for $0 \leq t \leq 40$ and explain the result. (e) Determine the capacitance of the second capacitor. (f) Determine the resistance of the resistor between the capacitors. (g) At $t = 40$ s, the second switch is closed as well. What will the currents through the circuit be and what the rates of change of the voltages of the two capacitors right after closing of S2? Assume the resistance of the second resistor to be equal to that of the first. (h) Sketch the voltages across the capacitors all the way to 80 s and explain your result.

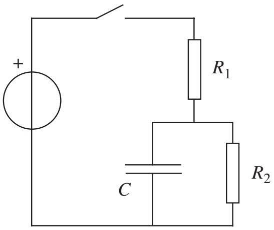

Figure P.8

8. For the circuit diagram shown in Fig. P.8, (a) sketch a hydraulic system made up of containers, pipes, and pumps which would be equivalent to the electrical system shown here; (b) write down the equations governing the processes taking place in the circuit. Solve the differential equation for the current through the second resistor and demonstrate that the time constant of the system is equal to $\tau = CR_1R_2/(R_1 + R_2)$.

9. An inventory contains a quantity M of a certain product. It is filled by a production rate P and drained by a sales rate S (the latter is assumed to be constant). There is a desired quantity (E) of the product in the inventory. When the stored quantity M differs from E, the production rate is changed. E is constant. Make the following assumptions regarding the change of P. The rate of change of P is proportional to the difference between desired storage E and the actual stored quantity M. We introduce a constant "inertia" or delay factor L to calculate the relation between inventory difference and rate of change of P (larger inertia leads to a smaller rate of change of P). (a) Sketch the diagram of a system dynamics model that represents the word model formulated above. (b) Formulate all equations of the model. Which equation is a law of balance? Which equation resembles an inductive relation? Which quantity is analogous to a pressure difference or a voltage? What is the unit of L? (c) What are the two differential equations of the model? What are the associated initial conditions? (d) Show that the two differential equations in (c) can be transformed into a single second order differential equation:

$$\frac{d^2M}{dt^2} + \frac{1}{L}M = \frac{1}{L}E$$

(e) What is the solution to the differential equation in (d) for $E = 0$? Is this the solution to a damped or an undamped oscillation? What is the period of oscillation? (f) What is the solution to the equation in (d)?

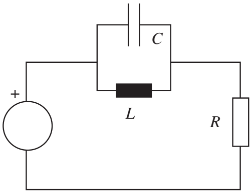

Figure P.10.1

10. The ideal power supply of the circuit shown in Fig. P.10.1 is turned on at $t = 0$. The voltage of the power supply is set to 10 V. The curves in the graph of Fig. P.10.2 show the electric currents through the branches containing the (ideal) inductive element, the resistor, and the capacitor.

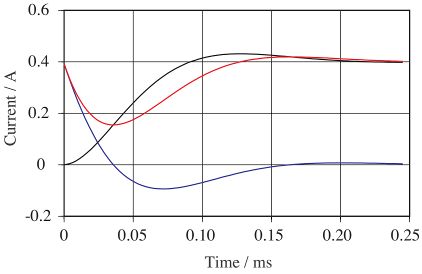

Figure P.10.2

(a) Show which curve in the graph belongs to which element in the circuit. (b) Use the data in the graph to determine the inductance, resistance, and capacitance. (c) Formulate all equations of the model of the circuit (including initial conditions). (d) Convert the model to a single second order differential equation for the voltage across the capacitor, including initial conditions.

CHAPTER 2

ENERGY IN PHYSICAL PROCESSES

So far we have not made use of an important aspect of physical phenomena. Whenever something happens in the physical world, processes are accompanied by an additional quantity—*energy*. We will see that energy plays a unique role, unlike the roles of quantities which are often mistaken for it such as electricity, motion, or heat.[1]

First, we will investigate chains of processes which teach us that a description in terms of amounts of fluids, electricity, or motion alone does not suffice: we need a property which quantifies the coupling of processes—namely energy. After this qualitative introduction, we will discuss quantitative measures for this new quantity by studying waterfalls, and hydraulic and electric processes. Then we shall take a closer look at energy transfer and energy storage. Finally, the description will be extended to rotational and magnetic phenomena.

2.1 ENERGY AND COUPLING IN CHAINS OF PROCESSES

Processes usually occur in chains. One process drives another, sometimes creating long chains. This phenomenon teaches us that there must be a physical quantity which relates one process to the next. We introduce energy to quantify the coupling of processes.

2.1.1 Processes Driving Other Processes

Examples of processes driving other processes are easy to find. Even limiting our view to hydraulic and electric phenomena we can identify coupling. In an electric water pump, we make use of an electric process to drive a hydraulic one (Fig. 2.1), and a

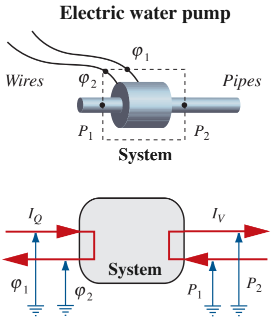

Figure 2.1: A process diagram of an electric pump shows an electric process driving the flow of a fluid. The electric process runs downhill, while the hydraulic process runs uphill. The pump couples the processes.

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[1] There are good reasons why we mistake other physical quantities for energy—at least in common sense reasoning. See Section I.2 in the Introduction for a brief discussion of this issue.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_3,

combination of turbine and generator couples a hydraulic process to the flow of electricity. If we extend our view and allow for additional processes such as rotation and heat, we find even more instances of coupling (Table 2.1): a rotational process drives the production of heat in the grinding of one mill stone against another; in a turbine, the flow of water drives a rotational process; and in the flow of a viscous fluid through a pipe the hydraulic process drives the production of heat (Fig. 2.2).

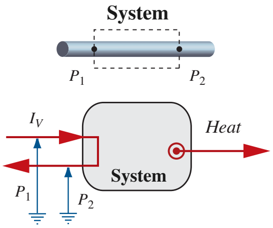

Figure 2.2: In viscous flow, the fluid flows from higher to lower pressure, driving the production of heat (notice the symbol of a source of heat).

Table 2.1: Examples of coupling of processes

	Hydraulics	**Electricity**	**Rotation**	**Heat**
Hydraulics	Hydraulic ram	Turbine plus generator	Turbine	Resistive flow
Electricity	Electric pump	Transformer	Electric motor	Electric heater Peltier device
Rotation	Hand pump	Generator	Gearbox	Friction
Heat	Solar water pump	Thermoelectric generator	Heat engine	Absorption refrigerator

Coupling of processes. A single process is quantified in terms of the two fundamental quantities used to conceptualize it: the fluidlike quantity and its associated potential. In hydraulic and electric processes, these pairs are volume and pressure, and electric charge and electric potential, respectively. These pairs of quantities are different for different processes—they are basically unrelated. Therefore, the question arises how different processes can be coupled. How can one process drive another in a determined manner? Two processes—such as an electric process driving a hydraulic one—must always be related or coupled in the same way. It never happens that the electric process drives the hydraulic process differently at different times. We expect a well defined relation between the two.

In other words, the same process should always accomplish the same result, assuming that conditions do not change. Therefore, we need a measure of how much a process driving another is accomplishing. We may also say that a process is *working* to accomplish a result. The measure introduced for “work” and “accomplishment” has to do with *energy*.

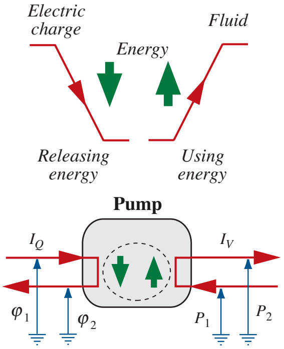

Figure 2.3: An electric pump couples electric and hydraulic processes. The driving process releases energy which is used (bound) in the follow-up process. The amount of energy released or used (bound) is the measure of how much processes “work” or “accomplish.” Release and binding of energy are depicted by fat vertical arrows.

Releasing and using (binding) energy. A voluntary process driving another process consists of water or electricity flowing through a potential difference from higher to lower levels. The reverse—involuntary—process consists of a fluidlike quantity being “pumped uphill” through a potential difference (Fig. 2.3, top).

Now we introduce the measure of how a process is working. We say that the driving process *releases energy* in the fall of the fluidlike quantity (Fig. 2.3, top) which is used to drive the follow up process, i.e., the pumping of another fluidlike quantity. In the latter case, we speak of the *binding of energy* to the quantity flowing “uphill.” Therefore, we can use the amount of *energy released* as the measure of how much a process works, and the amount of *energy used (bound)* for how much has been accomplished. Releasing and using energy is now introduced as an additional graphical element in the system diagrams depicting physical processes (Fig. 2.3, bottom).

2.1.2 Chains of Processes: Transferring Energy

Consider a chain of processes as in Fig. 2.4. Processes coupled in a device are like single links which can be connected to form long chains. Consider a turbine driven by a current of water, which drives a generator, which in turn can be used to drive the production of heat in an immersion heater (Fig. 2.4). Energy is not only the measure relating two otherwise unrelated processes in a device. The coupling of processes must work through long chains. While the coupling of two consecutive processes inside a device is the result of releasing and binding of energy when the first processes drives the second, two devices are coupled by the flow of quantities such as water or charge from one device to another (Fig. 2.4). Consider the coupling of the generator and the immersion heater in Fig. 2.4. In the generator, energy is bound to the current of charge flowing from lower to higher electric potential. In the immersion heater, energy is released in the fall of charge from higher to lower potential.

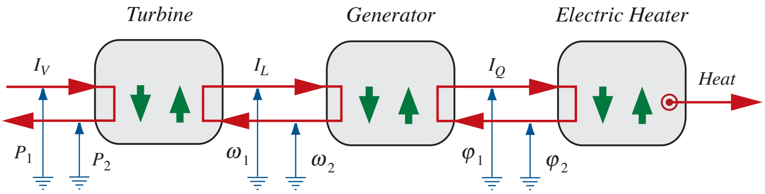

Figure 2.4: Processes can be joined in a chain. Flow processes provide for the coupling between devices or systems. (L is the symbol for angular momentum, the fluidlike quantity transferred in rotation; see Section 2.5.)

It seems to be reasonable to assume that the same amount of energy that was bound to the current of charge in the generator is released in the immersion heater. The second process perfectly reverses the first; electric current and voltage (potential difference) are the same. Therefore, we assume that the energy bound in the first process is transferred from the generator to the system following it (Fig. 2.5). In fact, whenever devices are coupled in processes, energy is transferred.

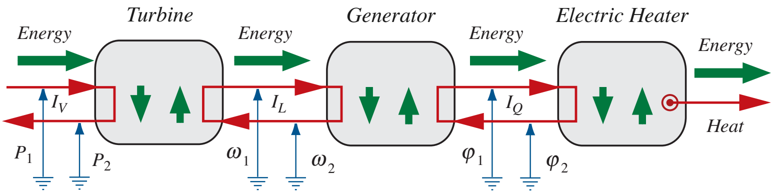

Figure 2.5: Energy is transferred from system to system together with the quantities exchanged in processes—such as fluids and electric charge. The transfer is depicted by fat arrows pointing from one system to the next.

2.1.3 Interrupting and Resuming Processes: The Storage of Energy

Chains of processes need not work continuously. It is possible to interrupt them, and resume them later or at some other place. Therefore, it should be possible to store the energy transferred through a chain so it can be used again for other processes.

Consider a pressure vessel which is being filled with a fluid with the help of a pump (Fig. 2.6). We need energy to operate the pump, i.e., we deliver it to the pump. It is released and used there and then transferred with the fluid to the pressure vessel. The vessel, therefore, is not only a storage device for fluids, but it also stores energy. We can use a pressure vessel filled with a fluid—and therefore with energy—to drive the operation of a turbine and generator, thus emitting the energy which was absorbed before by the vessel.

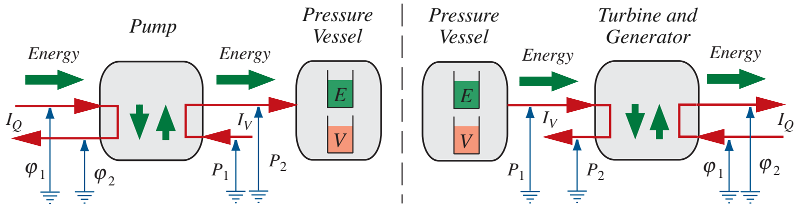

Figure 2.6: Chains of processes can be interrupted and then resumed later. This can be explained in terms of energy storage. The symbolic containers with letters *V* or *E* represent the storage of volume and energy, respectively.

2.1.4 Conservation of Energy: Can Energy Be Lost or Created?

Consider different electric pumps. If we drive them in an identical manner all the time, we expect the same result, which may be measured in terms of amount of water pumped to a given height. It is found that different pumps operate differently; some will pump less water than others.

Most processes in nature seem not to run at perfect efficiency—where the efficiency is measured in terms of the energy used in the desired process compared to the energy released by the driving process. Perfect efficiency would correspond to the case when the energy bound is 100% of the energy released. This is what we have assumed for all the processes depicted in the diagrams of Figs.2.3 to 2.6.

Does this mean that the lower quality pumps lose energy compared to the better ones? Actually, this is not the case. It is found that the engine drives two processes at once—the desired one, and an undesired production of heat—where each process uses part of the energy released. Together they use 100% of the energy available. What we have found to be true for pumps also holds for other processes. The apparent "loss" of energy is associated with an undesired production of heat which accompanies the process the engine was designed for (Fig. 2.7).

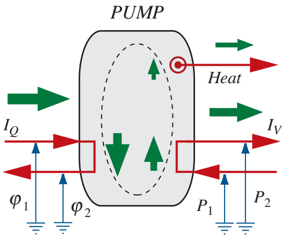

Figure 2.7: Energy is not "lost" in a process which does not run perfectly. Rather, the amount of energy which seems to be missing is driving an unwanted process—the production of heat.

There appears to be another reason for loss of energy. Energy storage devices usually lose some of their energy in the course of time. Again, we can explain this not as an actual loss but as the result of "leaking away" of energy. The energy which is not available any longer can always be detected in nature—at least in principle.

In summary, there is no reason to believe that energy can simply disappear. Neither can it be created. If we wish to set in motion a chain of processes, we always need an energy storage device which has to supply the energy running through the chain. Today we take this as one of the fundamental principles of nature: energy cannot be created, nor can it be destroyed: *energy is a conserved quantity*.

2.1.5 The Properties of Energy

Energy is a buzz word for much of what we read about in science and technology. Our usage of the term is often fuzzy which leads to imprecise images of what energy is all about. We usually speak of generating and losing energy, even though energy is conserved. We talk about converting energy, and we give it myriad names, even though there is only one type of energy: we speak of electrical, hydraulic, and mechanical energy, kinetic and potential energy, work and heat, and so forth. Most disturbingly, we mix up energy with the fundamental quantities flowing in physical processes, namely, electricity, heat, and motion.

Actually we have to learn very little about energy and what we learn repeats itself again and again in every field of physics. From what we have discussed so far, we recognize that there is just a single quantity called *energy* which accompanies all processes. This quantity has the following properties:

- Energy is released and used in processes.
- Energy can be transported from system to system.
- Energy can be stored in systems.
- Energy is conserved; it can neither be created nor destroyed.

The second and third items in the list make energy a quantity to which the laws of accounting can be applied; in other words, energy satisfies a *law of balance* (Section 2.4). The properties of energy will now be investigated more carefully and with quantitative means.

2.2 POWER: THE RATE AT WHICH ENERGY IS RELEASED IN A PROCESS

Nature presents us with a perfectly simple process which can serve as the archetype of physical processes—a *waterfall*. Other processes are interpreted analogously: a process consists of the flow a fluidlike quantity from a higher to a lower level (Fig. 2.3). We introduce *energy* as the measure of how much the fluidlike quantity is working, i.e., how much it can achieve, when it falls down a gradient of its potential. *Power* is the rate at which the fluidlike quantity is working. We will say that energy is released in a process, and power—the rate of working—is the rate at which energy is released. Common sense reasoning indicates that the power of a process will depend on the flow of the fluidlike quantity and the height of its fall.[2]

2.2.1 Power of an Electric Process

A simple experiment which can be used to quantify the measure of power is the electric heating of water. The rate of heating of water may be measured in terms of the rate of change of its temperature. If we always take the same amount of water at the same temperature, and observe the same rate of change of temperature, we can be sure that the electric process is "working at the same rate." In terms of energy we may say that this quantity has been released at the same rate in the immersion heater every time we repeat the experiment. On the other hand, if twice as much water can be heated at this rate, the electric processes must run at twice the rate.

Different runs of this experiment show that the rate of change of temperature is the same for identical bodies of water whenever the product of electric current through the

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[2] This is how Sadi Carnot expressed his idea of the power of heat. See the Introduction for a short discussion of his idea and the roots of common sense conceptualizations of phenomena and processes.

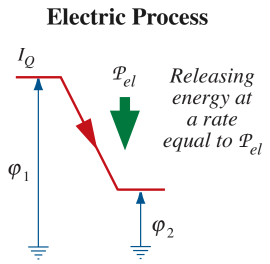


Figure 2.8: Energy released in an electric process. The rate at which energy is released (the power of the electric process) depends upon the flow of charge and the potential difference.

immersion heater and the electric potential difference across the device is the same. In other words, the rate of working of the electric process can be measured in terms of the product of electric current and voltage:

$$\mathcal{P}_{el} = -\Delta\varphi_{el} I_Q \quad \text{or} \quad \mathcal{P}_{el} = U I_Q \tag{2.1}$$

The symbol $\mathcal{P}$ is used for the rate at which energy is released; from now on we will call this quantity *power*. Therefore, we speak of the *electric power of a flow of electric charge*. The SI unit of power is the Watt (W). The minus sign in the first form of the equation is arbitrary. It means that the power of a voluntary process is counted as a positive number, while the power of an involuntary process is taken to be negative.

The equation can be interpreted graphically using the waterfall image of a process (Fig. 2.8). In an electric process that drives another process, electric charge flows "downhill" through a potential difference and in turn releases energy at a rate that depends upon the flow of charge and the potential difference in the simple manner indicated by Equ.(2.1).

2.2.2 Hydroelectric Power Plants and the Power of a Gravitational Process

We need a measure of the *power of a fall of water*, i.e., the rate at which energy is released in a gravitational process. By allowing water to accomplish a measurable result at a certain rate, we can define the power of a fall of water. Data on hydroelectric power plants yields the information we need (Table 2.2). If we take the product of electric current and voltage at the terminal of the generator as the measure of the rate of working of the water rushing down from the artificial lake to the turbine, we can see which factors determine the rate at which a waterfall releases energy.

Table 2.2: Examples of hydraulic power plants [a]

Hydraulic power plant	Current of Mass I_m / kg/s	Vertical fall of water Δh / m	Voltage and current [b] UI_Q / V · A	UI_Q / $I_m\Delta h$
Bavona	18,000	890	$137{\cdot}10^6$	8.6
Nendaz	45,000	1014	$384{\cdot}10^6$	8.4
Handeck III	12,500	445	$48{\cdot}10^6$	8.6
Chatelard	16,000	814	$107{\cdot}10^6$	8.2
Tiefencastel	16,700	374	$50{\cdot}10^6$	8.0

a. Hydraulic power plants with artificial lakes in Switzerland.
b. Product of voltage and electric current measured for the generator.

The results in Table 2.2 demonstrate that—except for an almost constant factor—the current of mass of water (measured in cubic meters per second) and the vertical drop of the water from the artificial lake to the turbine and generator station (measured in meters) determine the rate at which energy is released by the falling water. In fact, this quantity depends linearly on both factors. Doubling the current of water, or doubling the drop, will each lead to a doubling of the rate of release of energy.

Power of a waterfall. Specifying a waterfall first of all means quantifying the flow of water falling down. This is done with the help of the *current of (gravitational) mass* I_m (measured in kilograms per second). The second obvious quantity determining the properties of a waterfall is the vertical drop Δh (measured in meters).

The power of a waterfall, i.e., gravitational power, depends upon another parameter which is suggested by the fact that the strength of the gravitational field g must play a role. We expect the drop of water through a certain height to accomplish much less on the surface of the Moon than on the surface of our planet. Now we are ready to calculate the rate at which energy is released:

$$\left|\mathcal{P}_{grav}\right| = \left|g \Delta h I_m\right| \qquad \textbf{(2.2)}$$

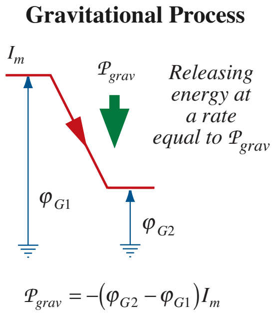


Figure 2.9: Energy released in a gravitational process. The rate at which energy is released (the power of the gravitational process) depends upon the flow of mass and the gravitational potential difference.

Potential. There is a simple graphical interpretation of the formula for the power of a waterfall (Fig. 2.9). We combine the first two factors on the right side of Equ.(2.2) into a new quantity which we call the *level* or *potential of gravitational processes*:

$$\varphi_G = g h \qquad \textbf{(2.3)}$$

According to the results in Table 2.2, g should be somewhat larger than 8 N/kg. We know from independent measurements that it is closer to 9.8 N/kg (Section 1.4.4). The discrepancy is a result of the imperfection of the processes in power plants.

We may now write the power of the process as the product of the difference of the gravitational potential and the current of mass falling through this difference of levels:

$$\mathcal{P}_{grav} = -\Delta \varphi_G I_m \qquad \textbf{(2.4)}$$

Note the analogy between this result and the one for electricity (Equ.(2.1)). The expression introduced for the gravitational potential is analogous to the one found in Chapter 1 (see Fig. 1.26).

2.2.3 The Efficiency of Processes

Note that the experimental determination of the factor in the last column of Table 2.2 leads to values that are a little bit smaller than g. This is due to the fact that the processes leading from the waterfall to the generator are not ideal: some of the energy released by the water is used for other purposes—mostly for the production of heat as a result of friction.

Ideally, all the energy released in a process would be used for the desired follow up process. Realistically, this does not happen, since parallel processes such as friction bind part of the energy released (Fig. 2.10). To measure the efficiency of the transfer of energy to the desired process, the ratio of the powers involved is used:

$$efficiency = \frac{\mathcal{P}_{desired\ process}}{\mathcal{P}_{driving\ process}} \qquad \textbf{(2.5)}$$

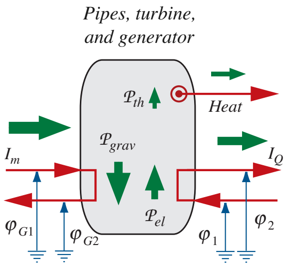


Figure 2.10: In a non-ideal coupling of processes, less than 100% of the energy released is used in the desired process.

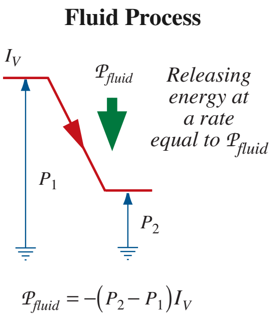


Figure 2.11: Energy released in a fluid process (hydraulic process). The rate at which energy is released (the power of the fluid process) depends upon the flow of volume of fluid and the pressure difference.

The power of an electric process is measured as the product of voltage and electric current (Equ.(2.1)). Applying this rule to the values presented in Table 2.2 we see that the overall efficiencies of modern hydroelectric power plants are quite high, of the order of 80% to 90%.

2.2.4 Power of a Hydraulic Process

Analogical reasoning suggests, and experiments confirm, that the type of relation found for the power of electric and gravitational potentials also holds for hydraulic processes:

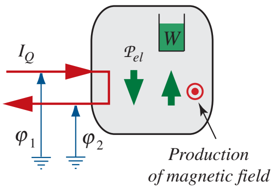
$$\mathcal{P}_{hyd} = -\Delta P I_V \tag{2.6}$$

Just consider a turbine driving an electric generator. The electric process is found to be identical as long as the product of the pressure difference and the flux of volume is kept constant. In summary, all types of processes investigated demonstrate the same basic structure (see Section 2.2.6 and Table 2.3): knowing one field of nature helps us to understand other subjects.

2.2.5 Power in Inductive Processes

So far, we have studied devices such as pumps, turbines and generators, artificial lakes and pipes, resistors, electric engines, etc. They all demonstrate that the release of energy is followed by its use when processes are coupled.

a. Increasing electric current



b. Decreasing electric current

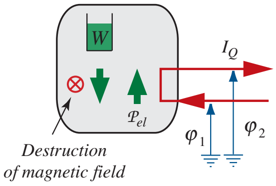


Figure 2.12: In an inductive electric process, energy is released or bound. The process is coupled to the creation or destruction of a magnetic field which acts as the storage device for energy in the inductive element.

Inductive elements (Section 1.6) seem to confront us with a somewhat different case. First, the other devices work strictly in one way—in resistors, volume or charge always flow “downhill”—while processes in inductors run both ways. Second, most of the systems mentioned before can run in steady state without involving the storage of energy; inductive devices, however, work dynamically only, and they also serve as energy storage devices.

Third and most important, it is not readily apparent if there are two processes coupled in such devices, one running “downhill”, driving the second one “uphill.” Closer inspection shows, however, that there are processes coupled to the obviously visible electric or hydraulic ones. Let us see what they are in the case of electromagnetic induction.

The phenomenon of electromagnetic induction is coupled to the growth or decay of magnetic fields due to electric currents. The magnetic field acts as the storage system for the energy (Section 2.4.5) which is released or bound by the electric current—depending on whether the current is increasing in time, or decreasing. If the electric current through an inductive device is increasing with time, i.e. if $dI_Q/dt > 0$, it runs “downhill” through the inductive potential difference $\Delta\varphi_L$ (Section 1.6). We have just learned that this process is associated with the release of energy at the rate

$$\mathcal{P}_{el} = -\Delta\varphi_L I_Q \tag{2.7}$$

There should be a process running “uphill” on the energy made available. This process exists: it is the building up of a magnetic field which at the same time acts as the storage device for the energy released in the electric process (Fig. 2.12a).

If the electric current through the inductive element decreases with time, i.e. if $dI_Q/dt < 0$, the magnetic field decreases as well, releasing energy which is picked up by the electric current. As a result, this current is driven "uphill" through the induced potential difference $\Delta\varphi_L$ (Fig. 2.12b).

The case of hydraulic induction is quite analogous. However, here we do not have a magnetic field associated with the current. Rather it is the quantity of motion of the flowing fluid which is built up or reduced in the device which acts similarly to the magnetic field.

2.2.6 Processes and Power in General

If a fluidlike quantity falls "downhill" it releases energy at a certain rate. This rate we call the *power* of the process. The energy that is released drives a follow-up process "uphill", and it is said to be used by or bound to the flowing quantity (Fig. 2.13). The law for the energy released or used is this:

> *The power of a process always depends on two factors—the potential difference and the current flowing through this potential difference:*

$$\mathcal{P}_X = -\Delta\varphi_X I_X \tag{2.8}$$

The letter X stands for the flowing fluidlike quantity which determines the type of process: mass, volume, and electric charge for gravitational, hydraulic, and electric processes, respectively (Table 2.3). For a given process, we have to use the proper fluidlike quantity and its associated potential. Thus, for a hydraulic process, X corresponds to V, and $\Delta\varphi_X$ corresponds to ΔP.

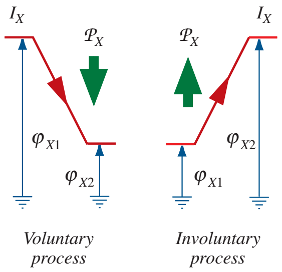


Figure 2.13: Processes and the power of processes. The same fundamental structure is discovered in all physical processes.

Table 2.3: Comparison of different processes

	Flowing quantity	Current	Potential	Potential difference	Power
Gravity	Gravitational mass	Current of gravitational mass	Gravitational potential	$\Delta\varphi_G$	$-\Delta\varphi_G I_m$
Hydraulics	Volume of fluid	Current of volume	Pressure	ΔP	$-\Delta P I_V$
Electricity	Electric charge	Current of electric charge	Electric potential	$\Delta\varphi_{el} = -U$	$-\Delta\varphi_{el} I_Q$ $= U I_Q$

Amounts of energy released or used in a process. Sometimes, we want to be able to say "how much has happened" in a process. In other words, we want to know how much energy has been released or bound as the result of a process lasting for a certain period. The amount of energy released in a process—which is sometimes called *work*[3]—can be obtained by integrating the power over time (Fig. 2.14). In general, this quantity can also be calculated as the product of the amount X_e of the fluidlike quantity flowing through a potential difference, and the potential difference $\Delta\varphi$:

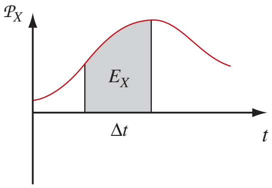


Figure 2.14: The integral over time of the power of a process yields the energy released or used in that process.

$$W_X = -\Delta\varphi_X X_e \tag{2.9}$$

This expression is correct only if the potential difference stays constant during the process. The relation is particularly simple to prove for a process running at a constant rate. The unit of energy (released) is the Joule (1 J = 1 W·s).

2.2.7 Electric and Hydraulic Circuits: The Balance of Power

An indication of the balance of energy comes from the consideration of energy released or bound in closed electric and hydraulic circuits: the sum of all terms of electric or hydraulic power add up to zero.

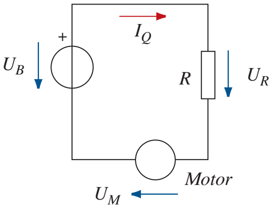


Figure 2.15: The sum of the potential differences in a closed circuit is always zero. Therefore, the sum of the electric power terms of all the elements combined must be zero as well.

This is a consequence of Kirchhoff's second rule which we encountered in hydraulics and electricity (Chapter 1). Consider a simple electric circuit containing a battery, a resistor, and an electric motor (Fig. 2.15). The current of charge flowing through all three elements is the same, and the voltages across them add up to zero:

$$U_B + U_R + U_M = 0 \tag{2.10}$$

The current is flowing through each of the elements leading to the release or binding of energy. If we multiply Equ.(2.10) by the current I_Q, we obtain $U_B I_Q + U_R I_Q + U_M I_Q = 0$. Since the terms represent the electric power in the elements, this is equivalent to

$$\mathcal{P}_{el,B} + \mathcal{P}_{el,R} + \mathcal{P}_{el,M} = 0 \tag{2.11}$$

This means that the energy bound in the electric process in the battery is equal to the energy released in the resistor and the motor combined as the consequence of the fall of the electric charge. In everyday language we say that the energy delivered by the battery is used by the resistor and the motor.

2.3 ENERGY TRANSFER AND ENERGY CARRIERS

Energy released in a process does not come out of the blue, and energy that is bound does not disappear. Either it is transferred into or out of the system or it comes from storage or will be stored (Section 2.4). Here we shall investigate the transfer of energy. There is a simple form of coupling of the flow of the fluidlike quantities with the flow of energy into and out of systems. It is as if mass, volume, and charge acted as *carriers of energy* in the processes they are responsible for.

2.3.1 Energy Carriers, Potentials, and Energy Currents

A simple example demonstrates how nature works. Consider the steady-state flow of a viscous fluid through a straight pipe as in Fig. 2.2. So far we have introduced the concept of energy in the following manner: since the fluid flows from a point of high

---

3. The words *power* and *work* are used inconsistently in different fields of physics. In mechanics, for example, work means a quantity of energy *transferred*, not released.

pressure to a point of lower pressure, energy is released in the hydraulic process at a certain rate (Fig. 2.16). The energy released is bound in the following thermal process. Remember that the production of heat due to friction is all that happens in the pipe; therefore, we assume that 100% of the energy released is bound in the follow up process.

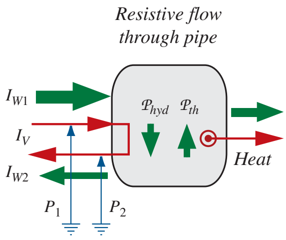


Figure 2.16: The energy released in the “fall” of fluid from high to low pressure must be supplied to the system. Energy is flowing into—and out of—the device with the fluid under pressure. The amount released and used flows out together with heat.

To be specific, let us introduce concrete numbers. Assume there is a fluid current of 0.10 m^3/s, and a pressure drop of 0.50 bar. According to Equ.(2.6), energy must be released at a rate of 5.0 kW. In other words, 5000 J energy are released each second and made available for the production of heat. We believe that the energy must be supplied to the system. Since the only possibility for this to happen is through the flow of fluid into—and out of—the pipe, we say that the fluid flowing under pressure carries with it some energy: we associate an *energy current* with the fluid (Fig. 2.16). In this sense we can call the fluid the *energy carrier* with respect to the system.

Naturally, we should expect the energy current to depend upon two factors. First, it must be proportional to the current of fluid; two equal currents under identical conditions will have twice the effect of a single one. Second, the pressure of the fluid must play a role. Let us see how energy and carrier currents are related.

If a fluid flowing into the system at a certain level (pressure) carries energy, so must the fluid flowing out of the system. Therefore, we assume that the rate at which energy is released is the difference between the currents of energy into and out of the pipe due to fluid flow. Since this makes the difference of the energy flows equal to the product of the pressure difference and the volume current, i.e.,

$$|I_{E1}|-|I_{E2}|=|(P_2-P_1)I_V|$$

the simplest expression for a single current of energy I_E is the product of the flux of volume and the pressure of the fluid as it enters—or leaves—the system:

$$I_{E,fluid}=PI_V \tag{2.12}$$

There is a simple image which can be used to remember this relation. We may look upon the pressure as the “load factor” of the “carrier current.” The current of volume is “loaded” with energy according to the value of the pressure. The flux of energy therefore is the product of a carrier current and its load factor.

Again, this is the structure of energy flow in all fields of physics. Consider the different devices and processes studied so far—gravitational and electric ones in addition to hydraulic: we always arrive at exactly the same relation for the expected energy currents.

> *The flux of a current of energy entering—or leaving—a system is the product of the flux of the carrier current and its associated potential (Fig. 2.17):*

$$I_{E,X}=\varphi_X I_X \tag{2.13}$$

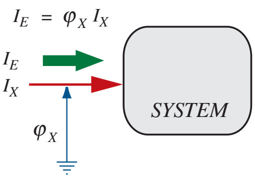


Figure 2.17: The relation of flux of energy, “carrier” flux, and the “load factor,” represented in a process diagram.

As we have seen in Chapter 1, the electric potential is not an absolute quantity. Values of electric potentials must always be measured with respect to a chosen level, i.e., the “ground.” The same is true for the gravitational potential; here on our planet we commonly measure levels or heights relative to sea level. Of the levels we know so far, only the hydraulic one is absolute. Fluxes of energy in electric and gravitational processes therefore do not have quite the same independent meaning as in fluid flow. Only the difference of two energy currents flowing into and out of a system together with a single current of a fluidlike quantity is independent of arbitrarily chosen levels. This difference is equal to the power of the associated process (Fig. 2.16).

This already tells us that the notion of energy being "carried" by the current of a fluidlike quantity should not bee taken too literally. In particular, as we shall see below, "carried" does not mean that the carrier current "contains" the energy being supplied. We should look upon Equ.(2.13) as meaning that energy always flows *at the same time* as the fluidlike quantity—rather than together with or directly bound to the carrier. It is certainly correct to state that *energy never flows alone*: at the same time, there must always be one or more flows of other physical quantities.[4]

2.3.2 Energy Transfer in Compression

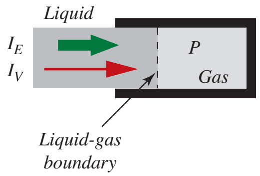


Figure 2.18: A gas in a vessel is compressed by a liquid flowing in. The gas has a pressure *P*.

There is an example of energy transfer that will play a particularly important role in our study of thermodynamics: energy flows associated with compression or expansion of a (compressible) fluid.

Imagine an imaginary wall separating a gas inside a container from a liquid that flows in or out so the gas is either compressed or expanded (Fig. 2.18). At the liquid-gas boundary we have a flux of volume of liquid at pressure P (which is the pressure of the gas enclosed by the liquid and the walls of the vessel). The current of volume of the liquid is I_V, so there is an energy flux $I_E = PI_V$ entering the gas. At the same time, the gas is compressed at a rate that equals the flow of volume of liquid. Since the volume of the gas is decreasing—we might say, volume of gas is "disappearing"—we describe the effect by a (negative) *production rate* of volume Π_V. In summary, a gas at pressure P being compressed at rate Π_V receives energy at the rate equal to

$$I_{E,comp} = -P\Pi_V \tag{2.14}$$

2.4 ENERGY STORAGE AND THE BALANCE OF ENERGY

In some sense energy is like amounts of water: we can account for it. We have seen this principle applied in the steady state processes investigated in the previous sections. Energy flows through chains of processes, and since we believe that it is a conserved quantity, we know that the flow does not change in magnitude.

---

[4] There is another point that needs to be taken into consideration. When we get into details of transport processes in later chapters, we shall see that there are three fundamentally different types of flows: conductive (flow through matter, caused by a potential gradient), convective (transport of a quantity stored in a fluid, as a consequence of fluid flow), and radiative (transport of a physical quantity with radiation). The relation between energy fluxes and fluxes of fluidlike quantities only holds for conductive transports. Conductive currents are those that are associated with their (own) potentials, so Equ.(2.13) (or Equ.(2.8), for that matter) make sense in this respect. A conductive current I_X is a current associated with or driven by the potential difference φ_X. As we shall see in Chapters 7 and 8, energy transfers in convection and radiation take different forms.

Changes in the flows in the course of time are possible, however, if energy is stored in systems. Only if we take into account storage of this quantity do we arrive at a general law of balance.

2.4.1 The General Law of Balance of Energy

Unless we believe that energy is either generated or disappears if chains of processes are interrupted, we must accept the idea that energy can be stored (Section 2.1). Bodies—and physical systems in general—can contain energy, and they can absorb it and emit it, thus changing the amounts stored.

As in the case of amounts of water—or amounts of electric charge—a law of balance relates what happens to the quantity stored as the consequence of flow into and out of the system. Because energy can neither disappear nor appear out of the blue, we know that amounts stored can only be changed as the result of flows. This is what we call the *law of balance of energy* for a system:

> *Energy can be stored and it can flow. The sum of all fluxes of energy* $I_{E,net}$ *with respect to a system tell us how fast the amount of energy stored will change:*
>
> $$\frac{dE}{dt} = I_{E,net} \tag{2.15}$$
>
> *(Fig. 2.19). This form holds for every moment. For a process lasting for a certain period, we may also say that the change of the amount of energy stored is determined by the total amount of energy* $E_{e,net}$ *transferred into or out of the system:*
>
> $$\Delta E = E_{e,net} \tag{2.16}$$

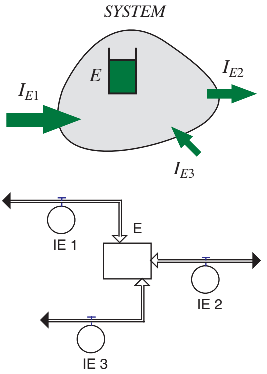


Figure 2.19: The law of balance of energy resembles the law of balance of amounts of water. The energy content of a system can only be changed as the result of flows of energy into and out of the system. Bottom: Graphical representation of the law of balance in a system dynamics diagram.

E_e is called an amount of energy exchanged as the result of a process. Note that one of the properties of energy—namely that it can be released and bound—does not appear in a law of balance. Releasing and binding take place inside the system being considered whereas a law of balance only speaks of the relation between amounts stored and amounts flowing into and out of the system.

2.4.2 Storing Energy with the Help of Gravity

We know how to calculate energy transfers. If we add to this the knowledge contained in the law of balance, we can determine changes of quantities of energy contained in particular systems. A particularly useful and graphically intuitive example is the storage of liquids in containers in the gravitational field. If we fill a tank with water, we add energy to the system along with the fluid, and this energy can usually be regained if the water is let flow out.

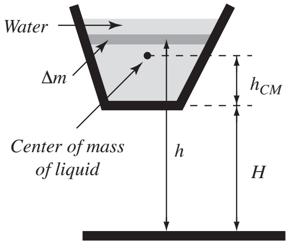


Figure 2.20: Water stored in an artificial lake contains a certain amount of energy relative to an arbitrary zero level.

Imagine a storage device such as an artificial lake having a certain shape. Water contained in it can flow down to a power station which is located at a certain level H below the bottom of the lake (Fig. 2.20). If we imagine a small amount of water having mass Δm at level h lowered to $h = 0$, the quantity of energy flowing out of the system is equal to $E_e = gh\Delta m$. This quantity is different for different layers of water in the lake. It is quite intuitive that, on average, all the water is lowered from the level of the center of mass of the liquid to the bottom. In other words, the water comes from an average level $H + h_{CM}$. The total energy that flows out, and therefore the change of the energy of the storage system, equals

$$\Delta E = g\left(H + h_{CM}\right)m \tag{2.17}$$

There is a special form of this for a straight walled tank sitting at level $h = 0$ and being filled to level h_0. With $H = 0$, $h_{CM} = h_0/2$, and $m = \rho A h_0$, Equ.(2.17) becomes

$$\Delta E = g\left(0 + \frac{1}{2}h_0\right)\rho A h_0 = \frac{1}{2}\rho g A h_0^2$$

Here, A is the cross sectional area of the tank. If we introduce a gravitational capacitance of the storage device:

$$C_G = \frac{\Delta m}{\Delta(gh)} = \frac{\Delta(\rho A h)}{\Delta(gh)} = \frac{\rho A}{g}$$

the former expression can be converted to

$$\Delta E = \frac{1}{2}C_G\left(gh_0\right)^2 = \frac{1}{2}C_G \Delta\varphi_G{}^2 \tag{2.18}$$

2.4.3 Storing Energy in Pressure Vessels

The derivation for the change of energy of a pressure vessel resulting from the change of volume of liquid stored in it, proceeds along similar lines to what we just did. Let me do it here in the general form. A pressure vessel is described by its elastance or its (hydraulic) capacitance $C_V(P)$ which, in general, is a function of pressure (see Section 1.4.2). If we add fluid to the vessel at pressure P, there is an energy current equal to PI_V accompanying the current of liquid. The integral of this energy flux over time equals the energy communicated to the tank which is equal to the change of energy stored:

$$\Delta E = \int_{t_0}^{t_f} I_E dt = \int_{t_0}^{t_f} P\dot{V}\,dt = \int_{t_0}^{t_f} PC_V\dot{P}\,dt$$

or, after a transformation of the integral,

$$\Delta E = \int_{P_0}^{P_f} C_V P\,dP \tag{2.19}$$

If we consider the case of constant capacitance, this results in

$$\Delta E = \frac{1}{2}C_V\left(P_f^2 - P_0^2\right) \tag{2.20}$$

Compare this to Equ.(2.18). We see that it is equivalent to what we obtained for a straight walled open tank in the gravitational field which corresponds to $C_G = \text{const.}$

2.4.4 The Energy Content of Capacitors

The derivation of the energy content (or the change of energy) of electrical capacitors does not add anything new. The result for capacitors having constant capacitance *C* is:

$$\Delta E = \frac{1}{2} C \left(U_f^2 - U_0^2 \right) \quad \textbf{(2.21)}$$

We can now summarize the results for storage of energy in simple gravitational, hydraulic, or electric systems having constant capacitances (see Table 2.4). Note that the results are given in terms of energy changes. Commonly, absolute energy contents are not known and are not needed, but we can always speak of an *energy content* relative to an arbitrarily chosen zero level.

Table 2.4: Capacitors with constant capacitance

	Gravitation	Hydraulics	Electricity
Capacitance	C_G	C_V	C
Potential difference	$\Delta(gh)$	ΔP	U
Stored quantity	$\Delta m = C_G \Delta(gh)$	$\Delta V = C_V \Delta P$	$\Delta Q = CU$
Stored energy	$\Delta E = 1/2 C_G \Delta(gh)^2$	$\Delta E = 1/2 C_V \Delta P^2$	$\Delta E = 1/2 C U^2$

2.4.5 Storing Energy in Inductors

Energy can also be stored in inductive electric and hydraulic elements. We can use Fig. 2.12a to demonstrate how to calculate the energy content of inductors. The derivation goes along the line of what we have seen in Section 2.4.3. The result for inductors having constant inductance is:

$$\Delta E = \frac{1}{2} L \left(I_{X2}^2 - I_{X1}^2 \right) \quad \textbf{(2.22)}$$

Here, I_X represents either the electric current I_Q or the current of volume I_V. In the electromagnetic case, the energy is stored in the magnetic field. In a fluid system, the energy is the energy of motion of the fluid.

2.5 ANALOGY ONCE MORE: SIMPLE ROTATIONAL MOTION

To demonstrate the power of analogical reasoning in physics once more, let us take a brief look at some simple phenomena from rotation. Now we can include the energy concept as well. If we restrict our discussion to the motion of bodies around a fixed axis, models turn out to be particularly simple, having a structure very similar to those we constructed for fluid and electric systems in Chapter 1.

Rather than developing a formal description of concepts of rotation, I shall limit myself to the construction of a few dynamical models. Ideas will be discussed and listed as we go along.

2.5.1 Rotational Collision of Two Flywheels

A simple phenomenon demonstrates the nature of rotation or, put differently, the source of a successful conceptualization of such phenomena. In an experiment, two plexiglass disks are mounted on the same vertical axis (Fig. 2.21). They are attached to the axis with ball bearings which allows them to spin more or less freely. The upper wheel can be lifted slightly from the lower one. If it is made to rotate, the lower one stays at rest. When the upper flywheel is let fall onto the second one, it interacts with it in a way that the former slows down as the latter spins up (Fig. 2.21, center).

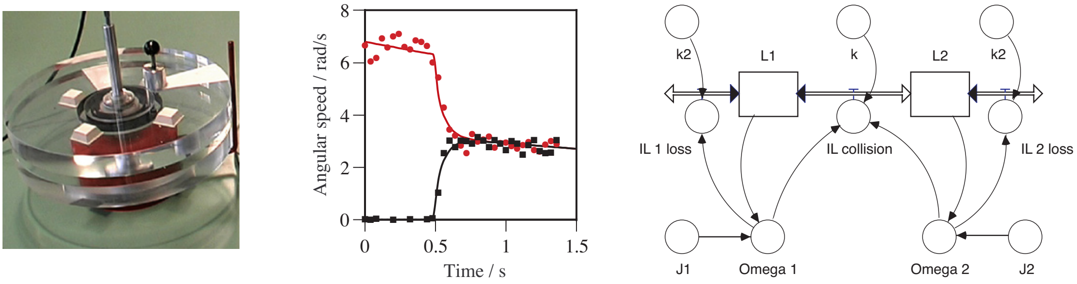


Figure 2.21: Two identical plexiglass flywheels rotate about the same vertical axis and interact (photograph on left). In an experiment, one wheel makes a second one spin up as it is slowing down (see the graph at the center which shows the angular speed of the wheels; dots: experimental data). Right: System dynamics diagram of a model of this system. Simulation of model: Solid lines in the graph (center).

Take a closer look at the data of the experiment in Fig. 2.21. The gross features are these. The upper wheel spins at constant rate—its angular speed is (almost) constant. When it touches the lower wheel, its angular speed goes down while the angular speed of the lower flywheel goes up. Within a very short period of time the angular speeds of the two wheels become the same, roughly half of the original speed. The wheels continue to spin at constant angular speed.

A second look confirms the first with the exception of the fact that angular speeds are not constant during the phases when the first wheel spins freely and when they spin together. During these periods, the angular speeds decrease.

This looks suspiciously like phenomena we have seen before in fluid or electric systems. Think about it—which simple fluid system would yield data similar to the one we have here? A little consideration reveals that the levels of a liquid in two communicating tanks each having an additional outflow will behave quite similarly.

All of this suggests that we can conceptualize rotational processes as follows. A spinning body possesses a “quantity of rotational momentum,” the more it has the faster it moves. This “quantity of rotational momentum” which is officially called spin or angular momentum can be communicated to other bodies through rotational interaction. The flow of angular momentum measures the strength of the interaction. So we expect a law of *balance of angular momentum* for a body:

$$\frac{dL}{dt} = I_{L,net} \tag{2.23}$$

L is the symbol for angular momentum (spin) and I_L denotes fluxes of this quantity. In the case of our experiment this means we should represent two storage elements for spin with their associated flows (Fig. 2.21, right). There is the flow of angular momentum from wheel to wheel and one flow from each wheel to the environment representing the effect of friction (we know that friction makes a wheel slow down):

$$\begin{aligned} \frac{dL_1}{dt} &= -I_{L,collision} - I_{L1,loss} \\ \frac{dL_2}{dt} &= I_{L,collision} - I_{L2,loss} \end{aligned} \tag{2.24}$$

We expect the fluxes of spin to somehow depend upon the speed of rotation. The speed at which a wheel spins is called angular speed. The simplest idea for a relation between spin and angular speed is

$$L = J\omega \tag{2.25}$$

ω is the symbol for angular speed, and J (the moment of inertia) is the measure of how much angular momentum a wheel needs to rotate at a given speed. The latter quantity is clearly analogous to a *capacitance* (Section 1.4.2). The intuitive meaning of angular speed is a *level*: levels adjust in communicating reservoirs. When Equ.(2.25) is applied to both wheels, the angular speeds can be calculated from the angular momenta.

This allows us to formulate ideas for the fluxes of angular momentum. If we simply apply the ideas from fluids or electricity, we might start with linear relations between flows and speed differences:

$$\begin{aligned} I_{L,collision} &= -k(\omega_2 - \omega_1) \\ I_{L1,loss} &= k_2\omega_1 \\ I_{L2,loss} &= k_2\omega_2 \end{aligned} \tag{2.26}$$

All we still need are proper initial values for the angular momenta of the two wheels. These are chosen according to the observed initial angular speeds. Choosing values for J and adjusting the flow constants k in Equ.(2.26), we can try to fit simulation results to data as in the graph of Fig. 2.21 (center). Clearly, the agreement between model and experiment is not bad at all. This does not mean, however, that we should already be satisfied with details of the model such as the forms for the flows in Equ.(2.26). Observations are not detailed enough to make a final judgement, but we can be sure that the structure of the model of rotational motion leads in the right direction.

We need values for the moments of inertia of the wheels to actually make the calculations, but we know that we can choose them arbitrarily—a change of J translates into a change of the flow constants k by the same factor. This means that, on the basis of considerations from rotational mechanics alone, we could arbitrarily define units for the moment of inertia or, equivalently, for angular momentum. However, rotation can couple to other phenomena and if these have been specified already, unit values must agree to make this coupling unique.

We have seen in this chapter that energy provides for a means of quantifying this coupling, so here is an example of the utility of the energy principle. Consider how we might apply this principle. Simply on the basis of analogy, we can formulate the expression for the energy stored in a spinning wheel; it should take the form found in

Table 2.4. Now we can write an expression for the balance of energy of the wheels before and after the interaction:

$$\Delta E_{i \to f} = \frac{1}{2}\left(J_1 + J_2\right)\omega_f^2 - \left(\frac{1}{2}J_1\omega_{1i}^2 + \frac{1}{2}J_1\omega_{2i}^2\right) < 0$$

The energy of the spinning wheels is smaller after the collision: energy has been released and used to produce heat. If we could measure the energy released, say by measuring how fast a body of water is getting warmer and comparing the result to what we know from how electricity warms the water (Section 2.2.1), we have additional information which lets us quantify the moment of inertia of the wheels.

2.5.2 Electric Breaking of a Flywheel

Here is a practical example that demonstrates the use of the energy principle in a dynamical model. A flywheel is attached to an electric generator (Fig. 2.22, left). It spins and drives the generator. If we hook up a resistor to the generator, the wheel will spin down as shown in Fig. 2.22 (right). As expected, the resistor will get warm. The angular velocity of the flywheel is close to an exponentially decaying function. (The angular speed is measured with the help of a second generator whose voltage is an indication of how fast the wheel spins.) Let us build a model for this experiment and experience how energy considerations become an integral part of the solution of the problem.

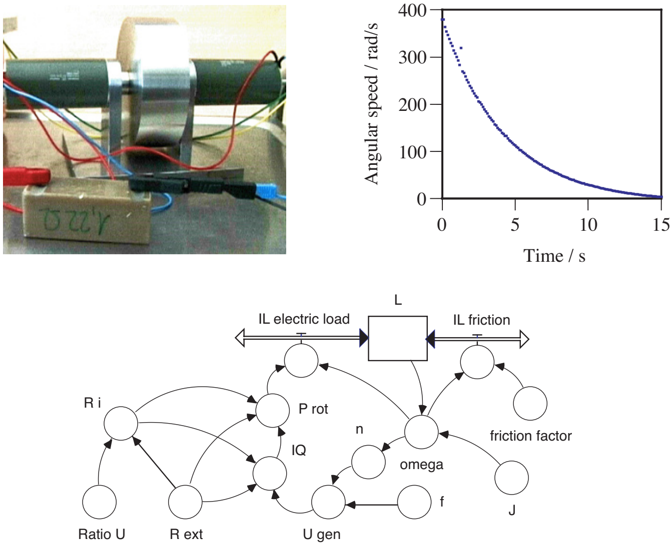


Figure 2.22: A flywheel drives a generator which is hooked up to a resistive load (top left). The angular speed decreases (top right). SD model diagram (bottom). n: number of revolutions per minute; f: conversion factor for rpm to open circuit voltage of the generator (U_gen); Ratio_U: ratio of open circuit voltage to voltage with load; R_ext: resistance of external load; R_i: resistance of generator; P_rot: rotational power of the flow of angular momentum.

The phenomenon reminds us of a container or an electric capacitor discharging. From the previous model in Section 2.5.1 we can be assured that the idea of discharging can be transferred to a spinning wheel as well. There are two phenomena affecting the behavior of the flywheel. First, the body would slow down even if we did not have a load connected to the generator. There is friction which, by the way, could or even should be quantified in an independent experiment. Then there is the effect of the electric circuit upon the rest of the system which can be best understood if we draw a process diagram of the devices making up the system (Fig. 2.23). The wheel emits angular momentum through the generator—this is why it decelerates. In the generator, the angular momentum flows from the high level, i.e., the angular speed of the spinning body, to the ground. If analogy can be used as a guide, energy must be released in this process which then drives the electric process of the flow of charge through the resistors in the circuit (there is the external load, but just as importantly, the wires making up part of the generator have and electric resistance as well). Energy is released in the electric process which is used to produce heat.

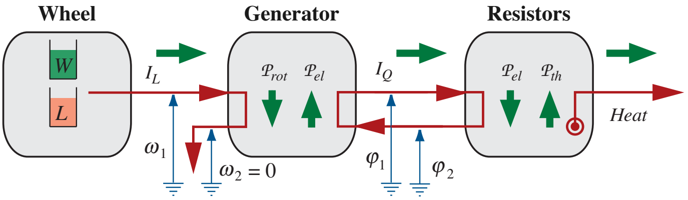


Figure 2.23: Process diagram of wheel, generator, and resistive load(s).

By applying the argument in reverse we can calculate the angular momentum flux from the wheel through the generator. The angular momentum of the flywheel lets us find the angular speed which converts to the open circuit voltage of the generator. With values for the resistances in the electric circuit we calculate the electric current. Finally, electric current and open circuit voltage of the generator yield the electric power which is equal to the rotational power. The important new idea that completes the model concerns the expression for rotational power:

$$\mathcal{P}_{rot} = -\Delta\omega\, I_L \tag{2.27}$$

By now we have become accustomed to formulating expression for the power of a process (Section 2.2). Rotation is not any different. If angular momentum flows through a difference of angular speeds, energy is released at a rate given by Equ.(2.27). The idea is visualized by the standard waterfall diagram in Fig. 2.24.

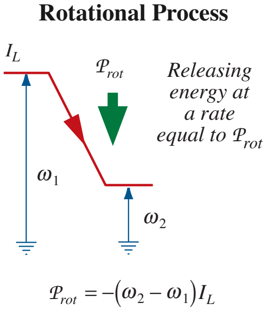


Figure 2.24: Energy released in a rotational process. The rate at which energy is released (the power of the rotational process) depends upon the flow of angular momentum and the angular speed difference.

2.6 THE EXCHANGE OF ENERGY IN MAGNETIC SYSTEMS

Consider the concrete example of a paramagnetic substance filling the interior of a long straight coil. If we turn on an electric current through the coil, a magnetic field will be set up which leads to the magnetization of the body inside. Naturally, this process involves the transfer of energy to the magnetized body.

It is known from electromagnetic theory that the rate of transfer of energy may be expressed in terms of the product of the *magnetic tension* U_{mag} and the Hertz *magnetic current* I_{mag}:[5]

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[5] Herrmann and Schmid (1986).

$$I_{E,mag} = U_{mag} I_{mag} \tag{2.28}$$

The magnetic tension and the magnetic current are defined as follows:

$$U_{mag} = \int_C \mathbf{H} \cdot \mathbf{s} dr \tag{2.29}$$

$$I_{mag} = \int_{\mathcal{A}} \dot{\mathbf{B}} \cdot \mathbf{n} dA \tag{2.30}$$

These definitions are similar to the quantities known from electricity. $\mathcal{A}$ and C stand for *surface area* and *curve*, respectively. The former is the path integral of the magnetic field **H**, while the latter is the rate of change of the magnetic flux. Obviously, the magnetic flux plays the role of the extensive magnetic quantity, and its rate of change replaces the rate of flow of electric charge in this analogy.

Let us now derive these quantities for the special example mentioned above. The magnetic tension in the uniform field of the coil is equal to

$$U_{mag} = LH \tag{2.31}$$

where L is the length of the coil. Since the magnetic flux density **B** is taken to be uniform over the cross section of the coil, the magnetic current turns out to be

$$I_{mag} = A\dot{B} \tag{2.32}$$

so that the magnetic energy current is equal to

$$I_{E,mag} = VH\dot{B} \tag{2.33}$$

With a paramagnetic substance in the field, the magnetic flux density may be expressed as follows:

$$B = \mu_o \left(H + \frac{M}{V} \right) \tag{2.34}$$

M is the total magnetization of the body. If we consider only the body as the physical system and neglect the field in empty space, the magnetic energy current associated with the magnetization of the paramagnetic substance is

$$I_{E,mag} = \mu_o H \dot{M} \tag{2.35}$$

There is an interesting point to be made about the example just treated and the compression of a gas (Section 2.3.2). The power involved in the compression of a simple fluid and in the magnetization of a body involves the production rate or the rate of change of an extensive quantity rather than the transfer of a quantity such as charge or mass. Obviously, there are physical processes in which quantities are not transported. Rather, they change their values directly at the locations where they are to be found. Such processes may be interpreted in terms of the creation or the destruction of the quantity involved. Production and destruction join transport processes in our description of nature.

EXERCISES AND PROBLEMS

1. Viscous oil is to be pumped from a shallow container into one lying 10 m higher up. The pipe has a diameter of 5.0 cm and a length of 20 m. If the mass flux is required to be 10 kg/s, how large should the power of the pump be? Draw the process diagram of the system and the processes. Neglect the acceleration of the fluid. Take values of 800 kg/m^3 and 0.20 Pa · s for the density and the viscosity of the fluid, respectively.
2. A large oil tank is filled through a pipe at its bottom (see Fig. P.2). The flow of oil is assumed to be laminar. (a) Derive the instantaneous power of the ideal pump in terms of the length and the radius of the pipe, the viscosity and density of the oil, and the height of the oil in the tank. (b) Express the energy needed to fill the tank up to a certain height in terms of the hydraulic capacitance. (c) Where has the energy that was supplied gone to?
3. If you fill the tank of Problem 2 through a pipe which leads to the top of the tank (Fig. P.3), how much energy is required? How does this compare to the results of those problems? Has energy been lost?
4. Derive the expression for the energy stored in a charged capacitor by considering the process of charging. Compare the result to the analogous hydraulic expression.
5. Consider two capacitors, one of them charged, connected in a circuit. (a) Calculate the final charges and voltages of the capacitors in terms of the initial charge and the capacitances. (b) Is the energy of the capacitors conserved? (c) Translate the problem into an equivalent hydraulic one.
6. A capacitor (capacitance 150 μF) and a resistor (resistance 1500 Ω) are connected in series to a battery (voltage 50 V) at time $t = 0$ s. The initial charge of the capacitor is equal to zero. (a) Derive the equation of balance of the charge of the capacitor. Derive the formula for the electric current as a function of time from its solution. (b) Draw the process diagrams for the battery, the resistor, and the capacitor. (c) What are the values of the electrical power of the three elements at 0.15 s? (d) What are the values of the corresponding electrical energy currents at that point in time? (e) Calculate the rate of change of the energy of the capacitor. (f) How large is the rate of change of the energy of the resistor?
7. A small photovoltaic panel consisting of 21 cells arranged in series is exposed to sunlight. (The surface area of a single cell is about 15 cm^2.) It is connected to a load resistor with variable resistance. Voltage and electric current for the load resistor have been measured for different values of the resistance (see Fig. P.7). Irradiation was about 60 W/m^2 for the first, 200 W/m^2 for the second, and nearly 400 W/m^2 for the third (the highest) curve. (a) Calculate the electric power of the panel for a voltage of 4.0 V for the three characteristic curves. (b) Determine the maximum values of the electric power for the three cases. What are the values of the load resistance for the maximum power point for the three curves? (c) Determine the efficiency of the panel for maximum power point conditions for the three cases.
8. Imagine an artificial mountain lake in the shape of a cuboid of 10.0 km^2 surface area, and 50 m depth. The turbine station of a power plant is located 150 m below the bottom of the lake. Assume that the lake can be filled and drained once a year. (a) How large is the energy stored with the water if we take the bottom of the lake as our reference level? (Assume the lake to be full.) (b) How large is the energy stored with the water if we take the turbine station as our reference level? (c) How large is the power of the water flowing out of the lake to the power plant if the lake is full? If it is almost empty? Take a flow of 20.0 m^3/s. (d) How much energy is released by the water flowing out of the lake and down to the power plant if the lake is drained completely once a year? (e) Now we cover the lake with photovoltaic cells. How much energy can we gain from them in one year if we assume the cells to have an efficiency of 10%.
9. Assume that 4 capacitors of 1.0 F capacitance each are connected in parallel. We want to charge them with the help of the photovoltaic panel of Problem 7 (Fig. P.9.1). The sun shines at 400 W/m^2 which yields the characteristic curve shown in the diagram (FIg. P.9.2).

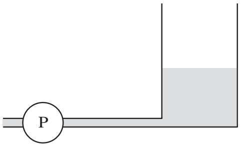


Figure P.2

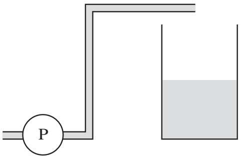


Figure P.3

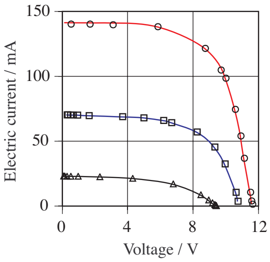


Figure P.7

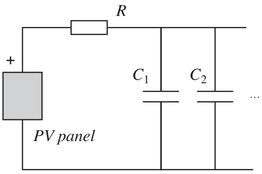


Figure P.9.1

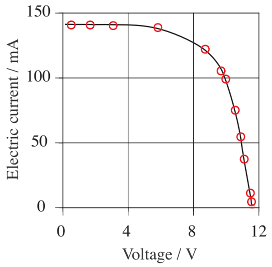


Figure P.9.2

A resistor is between the panel and the capacitors. (a) Choose the resistor so that if it were the only element in the circuit, we would have maximum power conditions. (b) What will the electric current be right at the beginning (when the capacitors are still uncharged)? What is the energy current flowing into the capacitors at that moment? (c) At a certain moment, the current through the circuit is 80 mA. What is the voltage across the capacitors at that time? What is the energy current flowing into the capacitor at that time? What are the electric power of the cells and the power of the resistor? (d) At a certain moment, the voltage across the capacitors is 5.0 V. What is the current through the circuit at that moment? (You will have to solve a set of nonlinear equations.) What will the energy current flowing into the capacitor be?

10. A large and shallow lake is going to be filled through a horizontal pipe with a length of 10 km. Initially, the lake is empty; in the end it is supposed to contain 10^5 m^3 of water. Assume the hydraulic resistance to be modeled by the law of Hagen and Poiseuille; i.e., take the volume flux to be proportional to the pressure difference across the pipe. The pressure drops by 10^2 Pa per meter of length at a volume flux of 1.0 m^3/s. While the lake is being filled, water evaporates from its surface at a rate of 0.10 m^3/s. (a) If the volume flux is constant and equal to 0.50 m^3/s how much energy is required for pumping while filling the lake? (b) How large should the (constant) volume flux be for the energy required to fill the lake to be minimal?

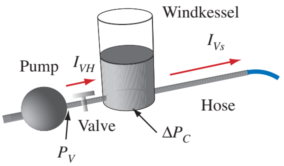
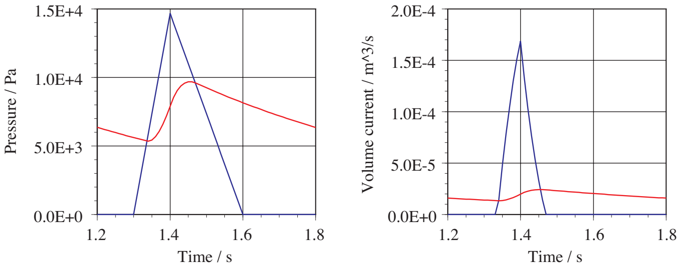


Figure P.11.1

11. Fig. P.11.1 shows a windkessel model of the systemic blood flow circuit. Resistances and capacitance are assumed to be constant. The capacitance of the aorta is $C = 2.0 \cdot 10^{-9}$ m^3/Pa. The resistance between pump (heart) and container (aorta) is $4.0 \cdot 10^7$ Pa·s/m^3, the one for the systemic vessels is $4.0 \cdot 10^8$ Pa·s/m^3. The diagrams (Fig. P.11.2) give data of a simulation of the model for one cardiac cycle of 0.60 s. In Fig. 11.2 (left), we see the pressure at the exit of the pump (P_V) and the capacitive pressure difference for the blood in the aorta (ΔP_C). The volume currents out of the heart (I_{VH}) and out of the aorta (I_{Vs}) are shown in Fig. P.11.2 (right). Data apply to the case of a sheep.

Figure P.11.2



(a) Identify the functions in the diagrams. (b) Determine the energy current associated with the blood flow from the heart and sketch the result as a function of time. Use this to determine the amount of energy flowing from the heart in one cycle. (c) How can the result from (b) be used to estimate the energy released in one cycle by the heart? What is a realistic value for the energy use of the heart of a sheep? (d) Determine the (lost) power for the flow from the heart to the aorta and use this to calculate the energy lost due to friction. (e) From when until when does the energy of the blood in the aorta increase? Determine the maximum change of energy of the blood in the aorta. (f) Formulate the law of balance of energy of the blood in the aorta in instantaneous form and add constitutive expressions to the equation.

12. Derive the expression for the energy contained in an inductive element (consider the process of starting a current flowing through a circuit containing a battery, an inductor, and a resistor). Translate the result for hydraulics. Show that you can obtain the formula for the inductance of a pipe with fluid by comparing the energy of the inductive element with the kinetic energy of the fluid in the pipe.

CHAPTER 3

TRANSPORT AND BALANCE OF MOMENTUM

Rotation and translational motion can be treated analogously to the theories of fluids and electricity presented in Chapter 1. This becomes particularly clear in single dimensional applications (motion along a straight line, rotation about a fixed axis; for the latter see Section 2.5). Momentum and spin (angular momentum) are stored in moving and rotating bodies, and they are exchanged with other bodies and the environment in mechanical processes. Naturally, there are many differences in detail between theories of motion and those of other fields. However, I am interested in aspects of the conceptualization that demonstrate deep similarities. It is interesting to see how far we can go in mechanics using ideas developed for fluids and electricity.

Apart from demonstrating the similarity between fluids, electricity, and motion, this chapter serves a particular purpose. I will present elements of the transport of momentum that go beyond what is known from fluids and electricity. Motion teaches us about conductive, convective, and radiative types of transport which will play a central role in a dynamical theory of heat.

3.1 PHENOMENA AND MODELS IN TRANSLATION

Similarly to how I proceeded in the case of rotation (Section 2.5), I shall introduce single dimensional translational motion informally by considering concrete phenomena and building adequate explanatory models for the processes observed. The aim is to create enough motivation for the image of a quantity of motion contained in moving bodies and communicated from body to body in mechanical interactions so that we are prepared for a more detailed discussion of transport phenomena (see Sections 3.2 – 3.4). Let me begin with the horizontal motion and collision of gliders on an air track.

3.1.1 Collision of Gliders With Magnets

Two gliders for an air track have been fitted with bar magnets that are oriented to repel each other (Fig. 3.1). The motion on the air track is nearly frictionless, so we can study the interaction of the gliders as they collide. One of the gliders has a larger mass than the other one. They are moving toward each other, come closer and then move apart

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_4,

without directly touching. The distance between the centers of the bar magnets has been measured from a movie of the motion (Fig. 3.1, center).

Let us conceptualize motion in terms of quantities of motion possessed by bodies in the manner already done by Newton. The faster a body, the more momentum it has; the heavier it is, the more momentum it possesses at a given speed. A mechanical process leads to the exchange of momentum. In the experiment, quantity of motion is clearly exchanged as a consequence of the magnetic interaction. Let us assume that this is all that is needed to explain what is observed.

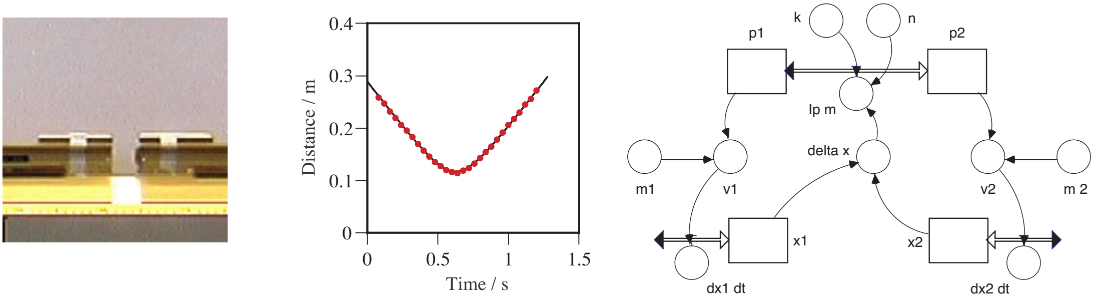


Figure 3.1: Two gliders on an air track, fitted with repelling magnets (left). The distance between the centers of the magnets has been measured as a function of time (dots, center) and simulated (solid line, center). Structure of a dynamical model (right). Note the representation of the balance of momentum of the gliders with a flow of momentum from one to the other representing the mechanical interaction. The elements denoted by x1 and dx1_dt symbolize the integration of the speed of a glider to yield a position (they are *not* laws of balance!).

Balance of momentum. As always, our dynamical model starts with an expression of laws of balance of the fluidlike quantities we envision behind the phenomena. Here, we have two possible repositories for momentum—the two gliders. As one of them moves to the right, it is given a positive quantity of motion; the other, moving to the left, obtains a negative amount of momentum. As they move closer together and the magnets begin to affect the motion, the first one slows down and eventually reverses its motion to the negative direction. The second one reverses its motion as well. Interpretation of the observation tells us that the first glider loses momentum whereas the second gains momentum. If we extend the interpretation, we are led to say that momentum flows through the magnetic field from the first to the second glider. In the model diagram (Fig. 3.1, right) we connect the reservoirs for momentum of the bodies by a momentum flow symbol. Expressed formally, we can say that

$$\begin{aligned}\frac{dp_1}{dt} &= I_{p,mag1}\\ \frac{dp_2}{dt} &= I_{p,mag2}\end{aligned} \tag{3.1}$$

where

$$I_{p,mag1} = -I_{p,mag2} \tag{3.2}$$

p is the symbol for the *momentum* of a body and I_p denotes a *flux of momentum* into or out of a body.[1] We may call the expression in Equ.(3.2) the *interaction law* in translational mechanics (remember the discussion in Section 1.1.2 which shows that the law of interaction is a general feature of our models of natural systems).

Capacitive relation. Everyday experience tells us that bodies interacting mechanically equilibrate their speeds (if friction dominates the effects leading to repulsion and oscillations). This is very much in accordance with what we know from all the other phenomena we have investigated so far. In other words, speed takes the role of the quantity that can be interpreted as the mechanical level (see Fig. 2.21 for rotation). If we continue this line of argument, we are led to postulate the same type of relation between stored fluidlike quantity and level (intensive) quantity, meaning that the momentum of a body should be proportional to its velocity:

$$p = m v \tag{3.3}$$

The factor of proportionality, the *inertial mass* of the body, is analogous to fluid or electric capacitances or to the moment of inertia in rotation (Section 2.5). Since the velocity of a body is given a sign depending upon the direction it moves in, momentum can take positive or negative values as well.

A force law. Now we have to construct a model for the flow of momentum from one magnet to another. Simple experiments with magnets tell us that the strength of repulsion grows with diminishing distance between them. We can try the assumption that the momentum current as a measure of the strength of the interaction grows inversely with some power n of the distance Δx_{CM} between their centers:

$$\left|I_{p,mag}\right| = \frac{k}{\Delta x_{CM}^{n}} \tag{3.4}$$

k is a factor measuring the intrinsic strength of the magnets, and n is some as yet undetermined exponent that describes the shape of the force-distance relationship for the magnets.

Kinematics. To complete the model, we have to find the positions of the gliders from their speed, and with that the locations of the centers of mass of the magnets. Positions are obtained by integrating the speeds (see the bottom part of the SD model in Fig. 3.1). In the model, the relations are expressed by saying that the velocities are the rates of change of positions:

$$\begin{aligned} \frac{dx_1}{dt} &= v_1 \\ \frac{dx_2}{dt} &= v_2 \end{aligned} \tag{3.5}$$

---

[1] If you are familiar with standard representations of mechanical phenomena, you may have already guessed that what has been called a momentum flux here is a force. Equ.(3.1) are Newton's expressions for the motion of bodies—his Second Law. The fact that the momentum current leaving the first body equals the momentum current entering the second is commonly called the Third Law or law of action and reaction. The relation between momentum fluxes and forces is a little more intricate than I put it here. Details will be discussed in the following sections of this chapter.

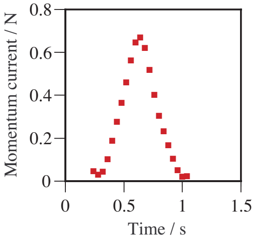


Figure 3.2: Magnitude of the momentum current during the collision (derived from data).

Simulation of the model. The equations of the model must be completed using initial conditions for the speeds and the positions, and by the masses of the gliders with their magnets. All these can be taken from the experiment. Once this has done, the model is complete and can be simulated. With data available, we can fit simulation runs to find best values for the interaction constant k and the exponent n. It turns out that $n = 5$ yields the best result. Fig. 3.2 shows the momentum current.

The energy of the gliders and magnetic field. The analogy between translational mechanics and fluids or electricity extends to the energy principle. Take the storage of energy in a moving body. According to Section 2.4, we should expect that

$$E_{kin} = \frac{1}{2} m v^2 \tag{3.6}$$

is the energy of a moving body. If we calculate the energy of both gliders together during the collision, we find that the sum is the same (long) before the collision and (long) after the collision (Fig. 3.3, left). During the collision, however, the energy decreases to a minimum after which it recovers to the original value. Since we believe that energy does not vanish, we should find another storage element that temporarily takes the missing energy.

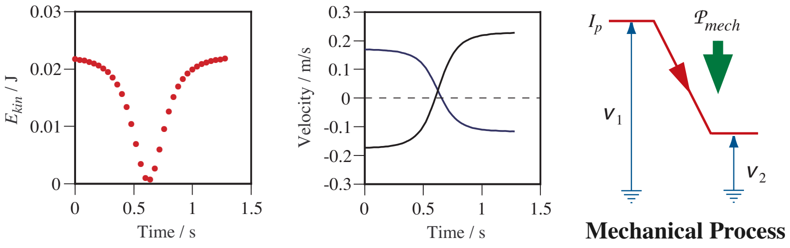


Figure 3.3: Sum of kinetic energies of the gliders as a function of time (left). Velocities of the gliders (center). Waterfall diagram of a mechanical process (right).

Let us reconsider what is going on with momentum during the collision. Momentum flows from glider 1 to glider 2. From Equations (3.1) and (3.2) we conclude that the rate of change of momentum of both gliders combined is always zero, meaning that their combined momentum is constant. Therefore, momentum simply flows through the magnetic field during the collision; nothing else happens to momentum, in particular, it is not stored in the magnetic field.

During the first half of the collision, the speed of glider 1 is higher than that of glider 2 (Fig. 3.3, center). So we have momentum flowing from a body of high to a body of low speed. Again, if analogy is a guide, we should conclude that energy is released during this phase (Fig. 3.3, right). During the second half of the interaction, momentum continues to flow from glider 1 to glider 2. This time, however, it flows uphill: the speed of glider 2 is now higher than that of glider 1. Momentum is pumped which means that energy is needed. It makes sense to assume that the energy released is used to strengthen the magnetic field and it is stored in the field—very much like in a mechanical spring. During the later phase of the collision, the stored energy is given back to the gliders, making momentum flow from the slower to the faster body. (Note that springs act like inductive mechanical elements: momentum flows through them and energy is released as long as there is a speed difference.)

3.1.2 Steel Ball Falling in Oil

Here is a second example of single-dimensional translational motion. A small sphere made of steel is let fall in rapeseed oil. The speed of the ball first increases and then levels off (Fig. 3.4, left). Understanding this phenomenon involves new ideas for types of momentum transfers. Beyond that, the model is standard (Fig. 3.4, right). There is an expression for the balance of momentum of the body, speed is calculated from momentum, speed and position are related by the well known kinematic rule, and momentum fluxes are expressed in terms of circumstances.

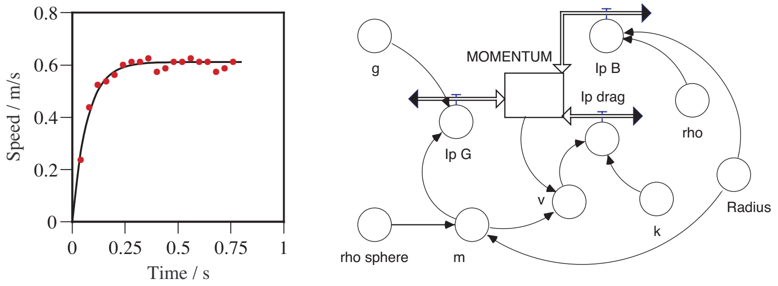


Figure 3.4: Vertical motion of a small sphere made of steel falling in rapeseed oil. Data of speed of sphere (left, dots) and simulation result (solid line). Diagram of dynamical model for the motion of the ball (right).

Momentum transfers. Since momentum flows as a consequence of mechanical interaction, we have to look for reasons for such interactions. We all are familiar with the effect of gravity upon the motion of bodies, and we know that touch can lead to the same results. There is a gravitational field, and there is oil touching the sphere. The former interaction leads to momentum transfer that is proportional to the gravitational mass m of the body:

$$I_{p,grav} = mg \tag{3.7}$$

where g denotes the strength of the gravitational field. If g is a positive quantity, the sign of Equ.(3.7) means that we count the direction downward as positive. Gravity supplies momentum to the body. Since gravitational and inertial mass are identical, we can use m to also calculate the speed from the momentum.

The case of the oil is a little more tricky. First, it is important to note that there are two types of interaction between steel sphere and oil. The first occurs only when the ball moves, the second takes places also when the sphere is at rest in the oil. The former is friction or *drag* which, most likely, depends upon the speed of the body in some manner. The simplest possible case is a linear relation of the form

$$I_{p,drag} = -kv \tag{3.8}$$

The negative sign means that, if speed is positive, momentum leaves the body; the sphere would slow down if drag was the only effect upon it.

The second effect of the oil has to do with pressure. Since the pressure of the oil increases downwards, the pressure upon the lower hemisphere of the ball is greater than that upon the upper hemisphere. The difference leads to what is commonly known as *buoyancy*:

$$I_{p,B} = -V_{sphere}\rho_{oil}g \tag{3.9}$$

Simulation. Using these ideas, the model yields very good results (Fig. 3.4, left). This does not mean that all the expressions are well chosen. Equ.(3.7) and Equ.(3.9) turn out to be adequate in just about all situations. Careful measurements reveal differences between actual situations and the assumption for drag made in Equ.(3.8). Drag depends sensitively upon the type of flow of a fluid around a body which is determined largely by flow speed and viscosity of the fluid.

The result of the model can be understood by analogy to a simple fluid system. Consider a straight-walled tank with a constant inflow of a liquid. The tank has an outlet. As we pour liquid into the tank, the outflow increases with increasing level of fluid in the tank. The resulting level as a function of time looks qualitatively like the speed of the sphere measured in this experiment. The levelling off is a result of an outflow that increases with increasing level—here it is the outflow of momentum due to drag that is assumed to increase with increasing speed. The effect of buoyancy is proportional to the effect of the weight of the sphere, so it does not change the appearance of motion. In summary, the equation of motion is

$$m\frac{dv}{dt} = \left(m - V_{sphere}\rho_{oil}\right)g - kv \tag{3.10}$$

3.1.3 A Water Rocket Train

As a last example, let us consider the motion of a water bottle rocket mounted on a toy train car moving on horizontal tracks (Fig. 3.5, left). It introduces a type of momentum transfer unlike the ones we have seen so far. This one has to do with a fluid transporting momentum across the system boundary which also leads to changes of the mass of the system; the phenomenon is called *convective transport*.

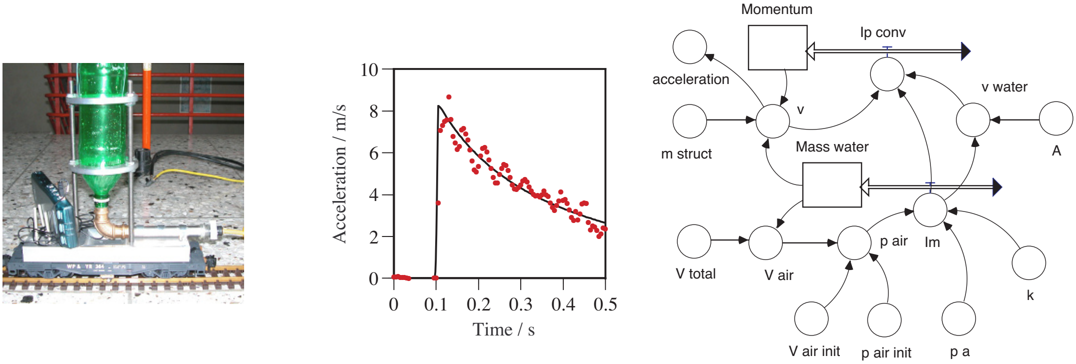


Figure 3.5: A water bottle serving as a rocket engine is mounted on a horizontally moving toy train car (left). Measurement (dots) and simulation (solid line) of the acceleration of the toy train (center). The diagram of the dynamical model (right) depicts two laws of balance: one is for the momentum and the other for the mass of the system.

Laws of balance. First, we have to make sure we know all quantities for which laws of balance have to be formulated. Since we are dealing with linear motion, we certainly have to analyze the balance of momentum. However, rockets are examples of so-called open systems that allow for the flow of matter across a system boundary. Our system is a moving control volume. The system boundary is an imagined surface around the car and bottle that is penetrated by the outlet pipe for the pressurized water.

There is a single flow of fluid which we can symbolize by a single current of mass of fluid I_m. There certainly are several momentum fluxes for the horizontal motion (not to speak of those for the vertical component). However, if we neglect air drag and friction, there remains a single momentum current associated with the flow of water. If we take the motion of the train as the positive direction of space, the water ejected obviously flows in the negative direction giving it negative momentum. Therefore, negative momentum leaves the system which means that positive momentum enters: the train will accelerate in the positive direction. In summary, the laws of balance are

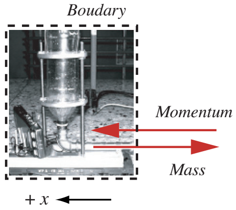


Figure 3.6: Open (flow) system with system boundary and fluxes of mass and momentum.

$$\frac{dm}{dt} = I_m \tag{3.11}$$

$$\frac{dp}{dt} = I_{p,convective} \tag{3.12}$$

A convective momentum current. The flux of momentum is due to the flow of fluid, and it will definitely be proportional to the flux of mass relative to the system. The other factor determining the momentum of the water jet is the speed of the water relative to the observer:

$$I_{p,convective} = v_{jet} I_m \tag{3.13}$$

(Since the mass flux is negative, and the flow is in the negative direction, the convective momentum current is positive.) The speed of the jet depends upon both the flow speed relative to the system and the speed of the system itself:

$$v_{jet} = v + v_{exit} \tag{3.14}$$

v_{jet} is the speed of the water relative to the observer, v is the velocity of the system, and v_{exit} is the exhaust speed of the water as it is expelled from the system.

Modeling the water flow. The hard part of the model is not so much the motion of the rocket but the flow of water out of the bottle. The water rocket works by having pressurized air on top of the water. When the valve is opened, the water is expelled by the expanding air. We need an expression for the pressure of the air as a function of its volume (the volume can be calculated from the remaining volume of water in the bottle which we obtain from the law of balance of mass). This actually necessitates knowledge of an interesting part of thermodynamics of gases which we are going to study in Chapter 5. At this point, let me just say that there is a relatively simple relation between volume and pressure of air in rapid expansion:

$$P = P_{init}\left(\frac{V_{init}}{V}\right)^{1.4} \tag{3.15}$$

which is different from what we could have inferred for the isothermal case discussed in Section 1.4.4. If we take a simple relation for turbulent flow driven by the pressure difference along the bent pipe (Section 1.4.1), we can complete the model presented in Fig. 3.5 (right).

Simulation. The results of the model are acceptable, at least qualitatively (Fig. 3.5, center). We now understand the motion of a rocket as the result of the convective momentum flux associated with the expelled fluid. Details of this experiment and the model are less convincing. There are many factors that are difficult to measure (such as the initial pressure of the air), and the flow of water is not easy to model. Measurement of the acceleration can be tricky as well.

3.2 STRESS AND THE CONDUCTIVE TRANSPORT OF MOMENTUM

In the following sections, I will provide a more detailed description of mechanical processes in terms of the transport of momentum. There are three fundamental modes of transport: *conductive* (which is related to mechanical stress), *convective* (due to the flow of fluids across system boundaries), and *radiative* (resulting from the interaction of bodies and fields).

3.2.1 Pushing or Pulling Bodies

By pushing and pulling on an object we transfer momentum to it. The momentum transferred comes from another system (us), or flows into some other body. Momentum may be stored in the system under consideration. If it is, the velocity of the bodies must change. It is possible, however, to leave the motion of the bodies unchanged, if we pull and push equally hard. In this case, the momentum supplied will again flow out of the system.

To avoid having to deal with three components of the vector of momentum, let us consider cases of pure tension or compression only. Consider the process of pushing a wooden block horizontally across a frictionless surface (Fig. 3.7). The block accelerates, which means that you supply momentum to it through your hand. You can feel the flow of momentum through your hand as compressional stress.

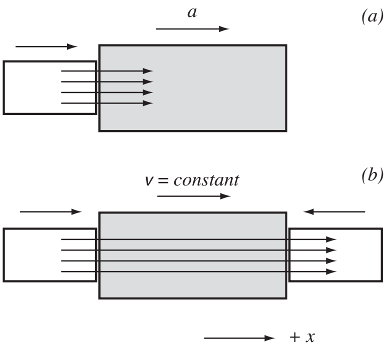


Figure 3.7: A block is pushed in the positive x-direction. It accelerates, which means that momentum is supplied to it (a). If we also push equally hard from the other side, the block's velocity remains constant (b). The momentum supplied from the left side has to leave at the right. In either case, momentum flows through the body itself. Note that in the case of compression, momentum flows through bodies in the positive direction. When momentum enters or leaves a body, we speak of a *flux of momentum* associated with the current.

Naturally, the momentum supplied must be distributed throughout the wooden block. You may convince yourself that this flux has nothing to do with the motion of the body itself: momentum, except for the part stored in the body, does not flow with the body. You may push equally hard on the other side of the block, in which case the block's velocity stays constant, while the momentum supplied at one end leaves at the other end (Fig. 3.7b). In other words, momentum may be transferred even through stationary bodies. This is called *conductive transport*. This term is known from thermodynamics, where we will encounter it again.

Summing up, we say that through direct contact, momentum may be transported across system boundaries and through matter. Conductive transport makes itself felt as stress. The flow of momentum across a part of a system's boundary is measured in terms of the flux of momentum I_p. If conductive transfer is the only mode of transport, the momentum stored in a body can only be changed due to a net conductive flux:

$$\dot{p} = I_{p,cond,net} \tag{3.16}$$

This is the *equation of balance of momentum* for this case. Remember that momentum is conserved. The conductive momentum flux is called a *surface force* F_s. Using this interpretation, we arrive at

$$\dot{p} = \sum_{i=1}^{N} F_{s,i} \tag{3.17}$$

which is a form of Newton's law of motion. Thus, Newton's law is a particular case of the general law of balance of momentum. So far it holds only for the case of conductive transport, i.e., only for surface forces acting upon a body.

3.2.2 The Continuous Case

If, with the help of constitutive relations, we manage to specify the fluxes of momentum with respect to a body, we can employ the law of balance of momentum and kinematic relations to calculate the motion of the body's center of mass. The momentum of a body is related to the velocity of its center of mass. Equ.(3.16) represents the overall balance of momentum for an entire body subject to surface forces. However, this is certainly not all that interests us in mechanics. For example, in the case of extended systems, we would like to know things such as the state of stress at every point inside a body. In other words, we view systems as being continuous, having properties that vary throughout space. Here, we shall give only a qualitative description of what is a major subject in continuum physics. The mathematical treatment of simple cases of continuous processes is left to Parts III and IV. The example treated here is rather complex in detail, however, it can be understood on a qualitative level.

The flux of momentum across a system boundary represents only a small part of the information contained in the actual transport process (Fig. 3.7). The current of momentum is distributed over the surface, and there is a spatial flow pattern inside the body. We must somehow be able to specify the spatial distribution of the flow, to fully describe the continuous situation. To this end, a quantity related to momentum currents appropriate for continuum physics is introduced, namely the (surface) *momentum current density* j_p. In the simplest case of a uniform flow of momentum perpendicular to a surface, the product of the current density and the surface area delivers the flux of momentum through the surface:

$$I_p = A\,j_p \tag{3.18}$$

The momentum current density is commonly called *stress* in mechanics. Pressure, for example, is the momentum current density in a fluid at rest (or what you measure if you flow along with the fluid).

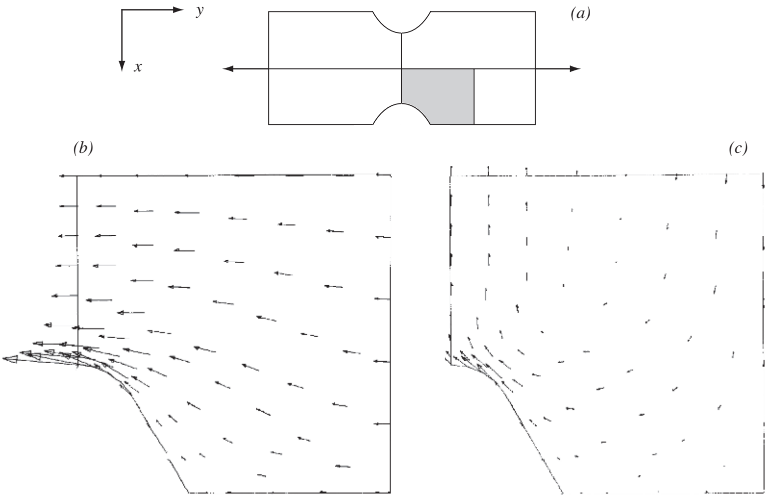


Figure 3.8: A flat strip of metal (a) with a notch on either side is set under tension. The two-dimensional stresses are represented by the flow patterns of two components of momentum (*x* and *y*) through the body. The shaded region was been analyzed by the finite element procedure. (b) *y*-momentum is flowing in the negative direction, demonstrating tension. The notches lead to a channeling of the flow, with higher current density (higher stress) near the notch. (c) Transport of *x*-momentum has been induced by the sideways flow of *y*-momentum. The FE computation was performed by K. Bruggisser and interpreted by W. Maurer (1989, 1990a).

Actually, the current density of every component of momentum is a vector which specifies the spatial distribution of the flow of momentum, just as velocity vectors may be used to visualize the flow pattern of water. In the general case we have to integrate the current density over a surface to obtain the flux through the surface. For every component, a flow pattern has to be drawn. We shall not treat the general theory here. Fig. 3.8 shows an example of a finite element computation which represents the stress inside a body as a flow field of momentum. Momentum current density vectors create the image of this field.

3.2.3 Viscosity and Momentum Transport

In this section we will discuss a particular example of a constitutive law. We shall encounter relations of the same general form again and again in continuum physics.

Viscosity is the property of fluids that leads to flow resistance. It is quite clear that the tank in Fig. 1.27 (top) drains more quickly if the oil is less viscous, and more slowly if the liquid is more viscous. Castor oil, for example, is much more viscous than olive oil, and olive oil is much more viscous than water. Therefore, viscosity critically influences the type of flow. Water flowing out of the tank in Fig. 1.27 would exhibit turbulent flow whereas the flow of oil through the same pipe under similar conditions would be laminar.

Consider a fluid such as oil between two large parallel plates (Fig. 3.9). We pull the upper plate horizontally, while the lower one remains stationary. If the fluid were ideal, the plate would simply slip on top of it. Since real fluids are viscous, however, they remain at rest with respect to the surfaces of bodies. In other words, the liquid will be pulled along with the moving plate. Naturally, the velocity of the fluid with respect to the lower plate has to be zero as well. Therefore, the magnitude of the fluid velocity changes from the speed of the upper plate to zero. There is a velocity gradient dv_x/dy in the y-direction.

The dynamical situation is as follows: Layers of the fluid move past each other which, because of viscosity, leads to friction in the fluid. We notice that we have to pull the upper plate if we want to maintain a constant velocity. Pulling the body in the positive x-direction implies that x-momentum is being supplied to it. In the steady state the plate does not store any more momentum than it needs for its motion, so we end up with a flow of momentum through the fluid from the upper to the lower plate. The lower plate conducts the momentum to the Earth. Here, we are confronted with the flow of a component of momentum not in its own direction but perpendicular to it: x-momentum flows in the y-direction. The fluid experiences *shear stress*. Note that shear stress, like tension or compression, is a case of conductive transfer of momentum. Momentum flows through matter, not with it. In the case being considered, the fluid obviously does not move in the direction perpendicular to the horizontal plates.

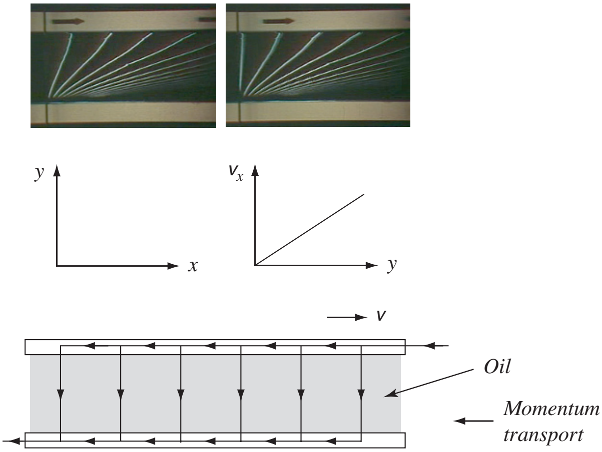


Figure 3.9: A viscous fluid is sandwiched between two large parallel plates. The upper plate is pulled to the right. Because of viscosity, the fluid does not slip at the solid surfaces. (In the photographs at the top we see bubbles being generated along a vertical line on the left moving to the right; they move faster the closer they are to the upper plate.) In the steady state, a velocity gradient is built up in the fluid. Momentum which is being supplied to the upper plate flows through the fluid from points of higher to points of lower velocity. In the simplest case, a constant gradient is established

The flow of momentum is properly described by its current density. Imagine x-momentum to be akin to some kind of “stuff” which may flow in any direction. Momentum is transported down through the liquid from every point of the upper plate. The distribution of the current over a horizontal surface is given by the momentum current density, which represents the shear stress. This quantity is the y-component of the current density vector of x-momentum, which may be abbreviated j_{pxy}. (This is the negative shear stress component τ_{xy}.) Now, a constitutive relation for viscous flow should allow us to relate this flux density of momentum to the kinematics of the flow and the properties of the fluid. Put differently, we are looking for a law relating the velocity gradient, the viscosity of the fluid, and the momentum current density j_{pxy}.

A good number of common liquids and gases exhibit a rather simple constitutive relation for viscous flow. The shear stress, i.e., the momentum flux density, is proportional to the gradient of the velocity in the fluid:

$$j_{pxy} = -\mu \frac{dv_x}{dy} \tag{3.19}$$

The coefficient μ is called the *dynamic viscosity* of the fluid. The minus sign appears since momentum flows (or is conducted, or *diffuses*) from points of higher speed to points of lower speed. The relation is called Newton's law (do not confuse it with the law of balance of momentum, or the law of gravitation, which also carry Newton's name), and fluids obeying this rule are called Newtonian.[2]

The combination of the constitutive relation for viscous momentum fluxes and the generic law of the balance of momentum allows for the computation of flow configurations. The law of Hagen and Poiseuille, for example, follows from the integration of the velocity profile established in steady-state viscous laminar flow through a cylindrical pipe. Qualitatively, the situation is as follows: the fluid is under pressure, which means that momentum is flowing through it in the positive direction; the pressure corresponds to the conductive momentum flux density in the direction of the axis of the pipe. Since the pressure is higher at the inlet, and since the fluid is not accelerated, momentum must be leaving sideways through the fluid. Because of viscosity, the fluid sticks to the walls of the pipe, leading to a velocity profile with a maximum magnitude at the central axis. Due to the radial velocity gradient, momentum is transported toward the wall, through which it leaves the system. A similar type of momentum flow is established if we pull a crate over the floor. We supply momentum to the crate. However, due to friction, momentum will flow vertically through the crate toward the floor. In a narrow layer between the crate and the surface it slides on, momentum flows from points which possess the speed of the crate to points whose speed is equal to zero (which is the speed of the floor). We know that the fall of a fluidlike quantity such as momentum from points of high potential to points of low potential releases energy (Chapter 2), and we know that this energy is used to drive a process, such as the generation of heat through friction (more about this the chapters on thermal physics).

3.2.4 A Comparison of the Conduction of Momentum and Charge

Viscosity is responsible for establishing velocity gradients in a fluid, and these in turn are responsible for the flow of momentum. We can compare this situation to what happens in an electric conductor such as a piece of wire. Charge is conducted through the wire as a result of the gradient of the electrical potential: charge flows "downhill" from points of higher to points of lower potential. The constitutive law appropriate for this transport is Ohm's law. Commonly, it is written in the form $I_Q = U/R$, where R is the electrical resistance. However, this is the definition of the resistance, rather than a constitutive relation. Ohm's law actually establishes the relationship between the flux of charge, the properties of the conductor, and the electrical driving force responsible for the flow. It is found that wires with twice the cross section simply conduct twice the charge. This suggests that the flux per unit surface area, i.e., the charge flux density, is equal in conductors of different cross section as long as all other factors are kept constant. Therefore, the flux density j_Q must be expressed by a constitutive law. If the flux density is proportional to the gradient of the electrical potential, the resulting re-

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[2] Bird, Stewart, and Lightfoot (1960), Chapter 1.

lation is called Ohm's law:

$$j_Q = -\sigma \frac{d\varphi_{el}}{dx} \quad \textbf{(3.20)}$$

Here, x is measured in the direction of the transport of charge, and σ stands for the electrical *conductivity*.

Compare this to Newton's law of viscosity in Equ.(3.19). Obviously, the viscosity has the meaning of a *momentum conductivity*. The higher the viscosity of a fluid, the better it conducts momentum down the velocity gradient. It is interesting to note that the temperature dependence of the viscosity of water is similar to that of the electrical conductivity of superconductors. Both increase with decreasing temperature and both make a sudden jump to virtually infinite values at a critical temperature (Fig. 3.10). Electrical conductors may become superconducting below the critical temperature, while water becomes a superconductor for momentum when it freezes! In both cases a phase transition is responsible for the abrupt change of properties. In mechanics this viewpoint might appear unusual, but it agrees with the facts. In electricity and in mechanics, charge or momentum flow, respectively, without a potential difference in the superconducting state. Indeed, in static mechanical situations, momentum is conducted through bodies without the bodies moving at all. And in both cases, the transport phenomena are non-dissipative: they do not produce any heat.

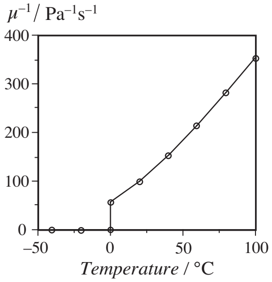

Figure 3.10: Reciprocal of the viscosity of water as a function of (Celsius) temperature. Since the viscosity is the momentum conductivity, its inverse is a resistivity. When water freezes, the resistivity goes to zero, just like the electric resistivity of a superconductor.

3.3 BODIES AND FIELDS: RADIATIVE TRANSPORT OF MOMENTUM

Mechanical interactions of a body with its environment do not just take the form of direct contact with other bodies. Bodies can interact indirectly via fields. In such cases, the direct interaction is between bodies and fields.

3.3.1 Sources and Sinks of Momentum

Consider the simple example of free fall in a homogeneous field, which can tell us much about the form of the transfer of momentum. It is clear that the body receives momentum (if we count the direction of free fall as the positive one). Experience also tells us that every part of a body will experience the same acceleration independently of density and composition. This means that a particular part of a body does not push or pull on other parts while in free fall. In other words, the interior of a freely falling body does not experience mechanical stress. Since stress is associated with conductive flow of momentum *through* matter, the absence of stress tells us that momentum cannot be transported *through* the body in free fall. Rather, every part of a body must receive momentum at the rate necessary for its acceleration.

Since the parts of a body receiving momentum are of arbitrary size and shape, and since there is no exchange of momentum between them, it is clear that momentum simply appears inside the body at every point without being transported there through other parts. This means that there are *sources of momentum* in the body itself. Momentum appears in a body at a particular rate quantified by the *source rate* Σ_p. The case of gravitation tells us that the source rate for a given part depends upon both the strength of the gravitational field and the gravitational mass of the part in question. This is the well known relation giving the weight of a body in terms of its gravitational mass:

$$\Sigma_p = mg \tag{3.21}$$

in a coordinate system pointing downwards. As always, g denotes the strength of the gravitational field which is measured in N/kg.

How is momentum transported from a field to a body, or vice versa? First of all, momentum must come from, or go to, another body. As a consequence, it must be transported *through the field*. It enters bodies from the field, or bodies emit momentum to the field. Consider a charged body in an electrical field. It is known from electromagnetic theory that momentum flows through the field. Specifically, if there is no charge in a region of the field, momentum entering the region must leave again (Fig. 3.11a). If we place a charged body in this region of space, however, the body changes the field so as to make the net flux of momentum through the region nonzero (Fig. 3.11b). In other words, momentum disappears in a region of a field occupied by a body, but it appears in the body. There are sinks of momentum in the field and sources in the body, and vice versa. The interaction of bodies and fields takes the form of sources or sinks rather than surface currents. This is so since bodies and fields "touch" in three dimensions rather than in two as do ordinary bodies in contact. Both bodies and fields occupy the same regions of space at the same time. This form of interaction is well known in the case of the transport of heat. Due to radiation, heat may enter or leave bodies directly. For this reason I call this type of transfer of momentum *radiative*.[3]

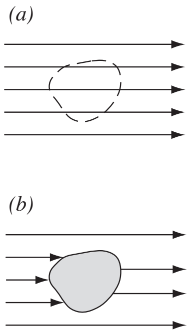

Figure 3.11: The total flux of momentum through a field is zero with respect to a region of space which is occupied by the field only (a). If we place a charged body in the electrical field, however, the situation changes (b). The body alters the field which leads to a net flux with respect to the region now occupied by charge. The change of the external field leads to the interaction of body and field.

The equation of balance of momentum for a body subject to surface and body forces must now include a source term with the fluxes of momentum:

$$\dot{p} = I_{p,cond,net} + \Sigma_p \tag{3.22}$$

This is Newton's law of motion including both *surface* and *body forces*:

$$m\dot{v} = F_s + F_b \tag{3.23}$$

since Equ.(3.22) only holds for a body which cannot change its mass. It is simply impossible to change the mass of a system if the only types of momentum transfer allowed are conductive and radiative in nature. Equ.(3.22) would be wrong in classical mechanics with the derivative of the momentum replaced by the ordinary derivative of the product of mass and velocity. (The resulting equation is not Galilean invariant.[4]) Obviously, cases with systems of variable mass must be treated differently; Section 3.4.)

3.3.2 The Tides

The example of bodies moving in a gravitational field nicely demonstrates the power of a qualitative solution of a problem in terms of flow patterns of momentum.[5] Con-

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[3] Fuchs (1987b,e), Herrmann and Schmid (1985), Heiduck, Herrmann, and Schmid (1987).

[4] Consider the equation from the point of view of another observer moving at speed v. The terms representing mass, acceleration, rate of change of mass, and sum of all forces are the same for all observers. The velocity multiplying the time derivative of the mass, however, is not. The problem was posed in this form by R. Resnick (RPI).

sider a thin rod falling freely in a field whose strength increases downwards (see Fig. 3.12). We found before that a body in free fall should not experience mechanical stress. This is true only for motion in a homogeneous field.

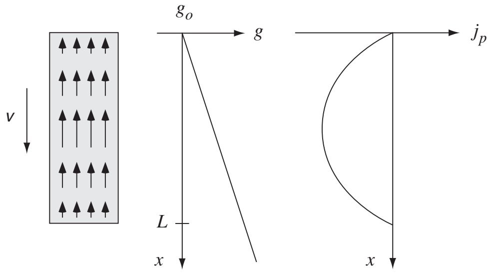

Figure 3.12: A long rigid rod falls in an inhomogeneous gravitational field. Tides are the result of such conductive rearrangement of momentum. Momentum flow is indicated by arrows in the rod. If g varies linearly, the stress, which is measured by the momentum current density j_p, is a quadratic function shown in the second graph on the right.

We have concluded that momentum is supplied to every part of a body in a gravitational field. The rate of supply certainly is higher where the field is stronger. If we now consider the rod to be oriented along the field lines, we have to conclude that the source rate of momentum is larger in the lower portions of the rod. Consider the rod to be rigid, in which case every part of it experiences the same acceleration. Therefore, the lower half receives more momentum than is necessary for free fall, while the upper part receives too little. The body solves the problem by rearranging the momentum supplied from the field: it allows the surplus of momentum to flow upwards through the rod to achieve equal distribution. This transport is obviously conductive in nature. Momentum flows through matter in the negative direction (Fig. 3.12), leading to tension in the rod, which may pull it apart. This phenomenon is known as *tides*. In the case of the Earth falling in the gravitational field of the moon, we can see the origin of the two tidal bulges on opposite sides of the fluid sphere. We can even say that the effect of the tides will be largest in the middle of the rod, since all the momentum gathering in the lower parts for upward transport must cross through the center of the body. Beyond this point, the current density decreases.

3.4 THE TRANSPORT OF MOMENTUM WITH MOVING BODIES: CONVECTION

The problem mentioned at the end of Section 3.3.1 has a simple solution. Momentum can also be transported with moving bodies. Since momentum is stored in moving matter, the flow of water across a system boundary also transfers with it some momentum. This mode of transport is called *convection*.

Consider a homogeneous flow field (Fig. 3.13). The speed of the flow of water is constant over a surface perpendicular to the direction of flow. The flux of volume across the surface is equal to the product of speed **v** relative to the surface and surface area. If we multiply this quantity by the density of the fluid, we obtain the flux or current of mass (**n** is the vector normal to the surface):

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5. Fuchs (1987d).

$$I_m = -\rho A \mathbf{n} \cdot \mathbf{v} \tag{3.24}$$

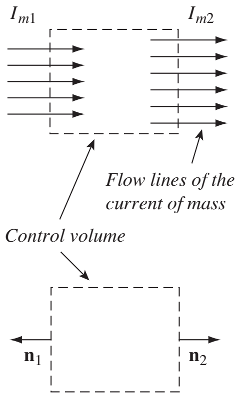

Figure 3.13: If matter is transported across the surface of a control volume, momentum is transferred along with it. This type of transfer is called *convective*.

The convective flux of momentum is simply obtained if we multiply this expression by the speed of flow:

$$I_{p,conv} = v_{fluid} I_m \tag{3.25}$$

where v_{fluid} is the speed of the fluid relative to the observer (which does not have to be equal to the speed relative to the surface of the control volume). If we wish, we can express the convective flux of momentum in terms of the transport of amount of substance, instead of mass. Now we can write the most general expression for the balance of momentum for a region of space such as the one in Fig. 3.13. The rate of change of momentum in this region must be equal to the sum of all fluxes of momentum, both conductive and convective, and the source rate:

$$\dot{p} = I_{p,cond} + I_{p,conv} + \Sigma_p \tag{3.26}$$

Here, *dp/dt* is the time derivative of the momentum contained in a control volume at a certain instant. It is not the time derivative for a body of constant mass. The problem mentioned after Equ.(3.23) is solved, since we now have a means for changing the mass of a system as a consequence of a particular type of momentum transfer. We simply have to extend Newton's law of motion to include convective momentum fluxes which are not present in the original formulation of the law. This is why it can be applied only to the case of bodies of constant mass. In fact, I shall use the term *body* in the sense of a portion of matter which is always identifiable and of constant mass. Consider a *body* to be a piece of matter surrounded by a surface through which mass may not be transported.

3.5 ENERGY IN MECHANICAL PROCESSES

The role of energy in mechanical processes is analogous to that known from fluids or electricity, so we can discuss the basics very briefly. Then there are some special aspects relating to what came up in this chapter that are worth looking into. These are the well known relation between energy and mass, the transfer of energy in the compression of a fluid looked at from the viewpoint of mechanics, and the question of energy transfer related to the different transfer modes of fluidlike quantities.

3.5.1 Energy in Translational Processes

Power. Momentum is the fluidlike quantity of translational motion and speed is the associated intensive quantity. Momentum can be transported and when it flows from points of higher to points of lower velocity, energy will be released at a rate defined by the momentum current and the difference of velocities:

$$\mathcal{P}_{mech} = -\Delta v I_p \tag{3.27}$$

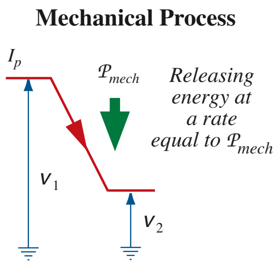

Figure 3.14: Waterfall diagram of a mechanical process. Momentum flows from points of high to points of low speed and energy is released.

Energy transfer. The case of energy transfer works quite analogously to the cases known from fluids and electricity as well:

$$I_{E,mech} = vI_p \tag{3.28}$$

This expression also applies to radiative transfers of momentum (bodies in fields). In cases of multidimensional motion we have to be careful of how we apply these relations (velocities and momentum fluxes are vectors, power and energy currents are scalars). The simplest way to think of this is to consider each component of motion in several dimensions separately. This is what we already did for the description of the flow of momentum through matter (Section 3.2.2).

Energy storage and balance of energy. Assuming a body subject to mechanical interactions (conductive and radiative momentum transfers), we can multiply the law of balance of motion by the speed of the body and then integrate over time:

$$\int_{t_1}^{t_2} v\dot{p}\,dt = \int_{t_1}^{t_2} v\left(I_{p,cond} + \Sigma_p\right)dt = \int_{t_1}^{t_2} I_{E,mech,net}\,dt$$

The last of these expressions is equal to the total energy transferred due to mechanical interactions. The first term transforms into

$$\int_{t_1}^{t_2} v\dot{p}\,dt = \int_{t_1}^{t_2} vm\dot{v}\,dt = \int_{t_1}^{t_2} vm\,dv = \frac{1}{2}m\left(v_2^2 - v_1^2\right)$$

which equals the difference of the *kinetic energy* of the body from beginning to end of the motion. If we accept that the kinetic energy is the energy of the moving body, the derivation presented is a proof of the law of balance of energy for purely mechanical phenomena. Here, I have simply reversed the standard argument that takes the balance of energy for granted and then derives other consequences.

Gibbs Fundamental Form. Consider a body receiving momentum and energy at the same time. From the balance of energy and momentum, together with Equ.(3.28), we have

$$\dot{E} = I_{E,mech} = vI_p = v\dot{p}$$

In summary,

$$\dot{E} = v\dot{p} \tag{3.29}$$

A relation of this type between rates of change of the energy of a system and the rate of change of relevant extensive quantities such as momentum, charge, or volume is called a *Gibbs Fundamental Form.*

3.5.2 Energy and Mass

Finally, let us discuss one of the most fundamental aspects of the nature of energy. Since the beginning of the 20th century it has been known that energy and mass (as a measure of gravity and inertia) are the same. This point will play a crucial role when it comes to the question of the nature of heat (Chapter 4).

The observations made so far about energy and momentum suggest a simple derivation of the relationship between mass and energy. Inertial mass is nothing but the momentum capacitance; i.e., it tells us how much momentum a body has for a given velocity. Now we will apply this idea to the phenomenon of light. As you probably know, light also carries momentum. Therefore, we may introduce the concept of momentum capacitance m of light, i.e. the quantity measuring the amount of momentum of the system divided by its speed c:

$$p = mc \tag{3.30}$$

The Gibbs Fundamental Form, Equ.(3.29), leads to the following expression for energy and momentum in the case of light:

$$E = cp \tag{3.31}$$

which is well known from the theory of electromagnetism. (c is the speed of light.) Combining both expressions finally leads to

$$E = mc^2 \tag{3.32}$$

So far this is not particularly important since it represents only the definition of the momentum capacitance of light. However, if we apply the idea which is embodied by Equ.(3.32) to normal bodies we end up with a very interesting result. If we assume the momentum capacitance (i.e., the mass) of bodies and of light not to be two different concepts we have to conclude that the mass of a body is another expression for its energy: mass, i.e., gravity and inertia, measures the amount of energy and vice versa. We may therefore write the relation between momentum and velocity as follows:

$$p = \frac{E}{c^2} v \tag{3.33}$$

If we set $v = c$ in the case of radiation, this result holds for bodies and light. We can use it in the calculation of the energy added to a body when its momentum is increased from zero to p. Substituting Equ.(3.33) into Equ.(3.29), we obtain

$$E\dot{E} = c^2 p\dot{p} \tag{3.34}$$

If we integrate this equation with values of the energy changing from E_0 (the rest energy of the body when its momentum is zero) to E (the corresponding amount of energy for momentum p), we end up with the general equation relating energy and the momentum of bodies and light, namely

$$E^2 = E_0^2 + c^2 p^2 \tag{3.35}$$

Again, this result also holds for light, since the rest energy of radiation is equal to zero. From this equation you may derive the expression for the inertia or gravity (i.e., the mass) of a body as a function of its velocity. Also, the classical expression for the kinetic energy of a body is the limiting case of the general relation if we allow only for velocities which are small compared to the speed of light.

3.5.3 The Compression of a Fluid

At this point, we will derive the expression for the transfer of energy which results from the compression or the expansion of a simple fluid. Consider a fluid such as air under pressure in a cylinder fitted with a piston (Fig. 3.15). In the rest position, momentum simply flows into and out of the system. Since the gas is not in motion, it does not have any stored momentum. Even though momentum is transferred into and out of the system, energy does not flow, since no part of the surface of the body of fluid is in motion.

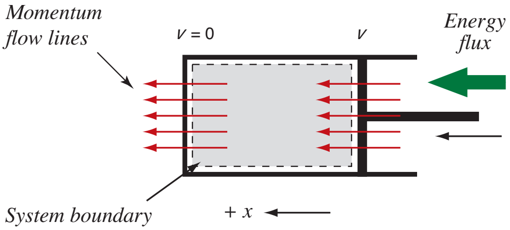

Figure 3.15: When a fluid is compressed, energy is supplied to the system as a result of the mechanical process. During expansion, energy flows out of the system.

If we begin to push the piston, however, the situation must change (Fig. 3.15). First of all, we are upsetting the previous balance of momentum. Now, during acceleration of parts of the fluid, the body will store a certain amount of momentum. If we then hold the speed of the piston steady, the momentum fluxes at the opposing faces of the cylinder will be equal again. Let us consider this situation. Only one part of the surface of the fluid is in motion, the part touching the piston. Since its speed is not zero, a flux of energy appears that is equal to the product of the speed of the surface and the flux of momentum across this part of the surface:

$$I_{E,mech} = vI_p \tag{3.36}$$

Since the momentum flux is equal to the product of the pressure of the fluid and the surface area of the piston, we may transform Equ.(3.36) as follows:

$$I_{E,mech} = vAP \tag{3.37}$$

This is equal to the product of the pressure of the fluid and the negative rate of change of its volume:

$$I_{E,mech} = -P\dot{V} \tag{3.38}$$

This result holds in general for fluids of any shape in three dimensions. Since the rate of change of volume of a compressible fluid is equal to the rate at which volume is produced or destroyed, Equ.(3.38) is equal to the expression derived in Equ.(2.14). We shall have ample opportunity to use it in the following chapters of the book.

3.5.4 Different Modes of Transport of Fluidlike Quantities

Care must be exercised in applying the relation between currents of fluidlike quantities, potentials, and the energy currents presented in Equ.(3.28). There are three fundamentally different types of transport processes for the fluidlike quantities, and Equ.(3.28) only holds for one of them. Even though we will learn details about transport processes in later chapters only, we should take a first look because of the importance for energy transfers.

Conductive transports. The transport processes considered in Chapters 1 and 2 are of a particular kind: they are the ones where a potential difference is required for a fluidlike quantity to flow by itself—a gravitational potential difference for currents of gravitational mass, a pressure difference for currents of volume, and an electric potential difference (voltage) for currents of charge. Let us take a closer look at the last of the three examples.

When electric charge flows through a conducting material, it does so on a “downhill” path from higher to lower electric levels (Chapter 1). Charge flows by itself *through* matter, not with matter. This type of transport is called *conduction* of electricity.

Even though it appears to be different at first sight, the flow of volume through pressure differences is of the same kind. It is true that here matter is flowing as well. However, this is not the important point. Amounts of fluids are flowing as the result of differences of their associated potential—pressure—and that is the hallmark of conductive transports. The same is true of gravitational processes: gravitational mass gives rise to gravitational fields and therefore to differences of the gravitational potential. Again, the flow of the fluidlike quantity is associated with its own potential.

Convective transports. Charge, for example, can be transported in a totally different manner. Rather than flowing through a conductor, it can be stored in a body. When the body moves, the charge it contains is also transported. The most important cases of this type of transport occur in fluid flow. Fluids can contain other fluidlike quantities such as charge, heat, or quantities of motion, so when the fluid flows, we do not only have a flow of amount of substance or volume, but also transports of these other quantities. Obviously, in this case, charge, heat, and motion do not have to flow by themselves through the fluid, they are transported *with* the fluid.

Such transports are called *convective*. Here, the flow of a quantity such as charge is *not* associated with a difference of the electric potential; charge flows because the fluid flows, and that is the result of a pressure difference! In summary, for convective transports of fluidlike quantities, we do not need the differences of their associated potentials.

> *Conductive transports of fluidlike quantities are associated with (differences of) their respective level quantities (Table 2.3). In convection, on the other hand, the driving force is the one for the fluid containing some other quantities which are carried along.*

Radiation. Finally, some of the fluidlike quantities can be transported through empty space with the help of radiation. Think of heat which flows from the surface of the Sun toward our planet. Radiation can contain—and therefore carry away—heat. Also, if the radiation is intercepted by a material body, it, and the heat it contains, can be absorbed. The transfer of radiation into a material system is of an altogether different nature than the transfer by conduction and convection. Radiation is absorbed inside bodies, not just at their surfaces. Just think of a glass sphere exposed to the light of the Sun. In other words, quantities such as heat may be brought directly into the interior of bodies with radiation without having to flow there through the material from the surface.

Energy transports. In all three transports of fluidlike quantities energy flows as well, but only in one case does the relation between currents and energy flow take the form of Equ.(3.28)—namely for *conductive* transports. All the other cases, convection, radiation, and absorption or emission of radiation, have to be studied separately.

3.6 DERIVATION OF THE WAVE EQUATION

By combining everything we have done so far, we can treat an interesting example that leads to a model of wavelike transports—the theory of transport of momentum in one direction through a simple conducting medium. We will see that wavelike transport is the result of the interplay of storage and transport of momentum, where the constitutive relation for the transport is given by an inductance, while the storage is described using the momentum capacitance of the system. This is in accordance with what was briefly discussed in Section 1.6.4 for waves in fluid and electric systems.

Imagine a fluid under pressure. Momentum is transported through it in the positive x-direction (Fig. 3.16). The equation of balance of momentum for this body is rather simple. We consider the boundaries of the body to move with the fluid, which means that there may be only conductive currents of momentum. Therefore, the law of balance takes the form

$$m\dot{v} = I_{p1} + I_{p2} \tag{3.39}$$

which is a special case of Equ.(3.16). Remember that the mass of the body is the momentum capacitance, and that the momentum current density j_p is the pressure of the fluid. Now, we shall introduce the momentum capacitance per length (mass per length) C'. If Δx and A are the length and cross section of the element of fluid in Fig. 3.16, the equation of balance of momentum becomes

$$C'\frac{dv}{dt} = -A\frac{1}{\Delta x}\left(j_{p2} - j_{p1}\right) \tag{3.40}$$

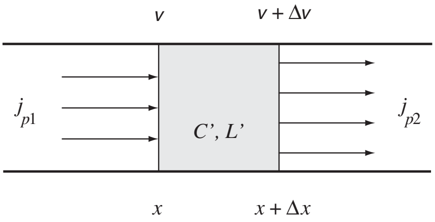

Figure 3.16: A fluid such as a gas is enclosed in a long pipe. Every part of the fluid possesses a certain momentum capacitance and momentum inductance. As a result, a disturbance leads to a transport of momentum in wavelike form.

The particular form of the transport depends upon the type of constitutive relation satisfied by the material. A body possesses resistance and inductance related to the transport of momentum. Both quantities are introduced in analogy to what we know from electricity or hydraulics. We shall neglect the resistance of the medium to the passage of momentum. (The phenomenon of resistance would lead to an attenuation of the wave traveling through the fluid.) To describe the other effect, the inductance per length L' will be introduced. The constitutive law of induction relates the difference of speed of the two faces of the body of fluid in Fig. 3.16 to the rate of change of the momentum flux through the body.

$$\Delta v = -L'\Delta x A\frac{dj_p}{dt} \tag{3.41}$$

This phenomenon results from the spring-like nature of the fluid: if there is a difference of speeds at the faces of the body, its density, and therefore its pressure, must change in time. Both Equations (3.40) and (3.41) must hold for arbitrarily small parts of the fluid. Therefore, these expressions become partial differential equations:

$$C'\frac{\partial v}{\partial t} = -A\frac{\partial j_p}{\partial x} \tag{3.42}$$

$$\frac{\partial v}{\partial x} = -L'A\frac{\partial j_p}{\partial t} \tag{3.43}$$

The former represents the balance of momentum for the continuous case, while the latter is the law of (momentum) inductance. We may combine these equations in the following manner. Take the time derivative of Equ.(3.42) and the spatial derivative of Equ.(3.43). In both expressions, derivatives of the momentum current density with respect to both time and space occur. Relating these terms leads to

$$\frac{\partial^2 v}{\partial t^2} = \frac{1}{C'L'}\frac{\partial^2 v}{\partial x^2} \tag{3.44}$$

which is a simple wave equation for transport in one spatial dimension. The term $C'L'$ represents the inverse of the square of the speed of sound in the fluid (Section 1.6.4). If we manage to determine the inductance of the fluid, we can also compute the speed of propagation of sound (Chapter 5).

The derivation of the wave equation for one-dimensional compressional waves can be carried over to other fields of physics, such as electricity or heat. In electricity, we may obtain the governing equation for a wave guide (telegrapher's equation). Inclusion of the resistance of the medium leads to the term responsible for dissipation and attenuation of the wave. In thermodynamics, the result equivalent to this particular form of Equ.(3.44) is not generally known. However, the phenomenon of thermal induction exists and leads to interesting results, such as second sound (see Chapter 13).

EXERCISES AND PROBLEMS

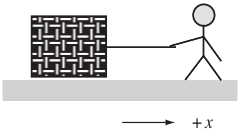

Figure P.1

1. A person is pulling a crate across the floor at constant speed via a rope (Fig. P.1). Take the positive direction to coincide with the direction in which the body is pulled. (a) Identify the closed circuit through which the horizontal component of momentum is flowing. (b) Determine the momentum fluxes (and their signs) with respect to the crate, the person, and the earth, i.e., the floor. (c) There are several relationships between the different fluxes identified in (b). Which of these have to do with the action-reaction principle (Newton's third law)? Which condition is expressed by the other relationships?
2. Repeat the previous problem with the positive x-direction reversed. Note that the closed momentum current changes its direction while the fluxes change their sign. How could you turn the expression for the momentum flux in Equ.(3.18) into a vector concept? If you draw the fluxes in this and the previous problem as vectors, do they change direction upon changing the sign of the x-coordinate? What is the relationship between the momentum flux vectors and the forces customarily introduced in this mechanical situation?
3. A body with a mass of 2.0 kg is hanging from a rope. Take the downward direction as the positive one. Determine the fluxes and the sources of the vertical component of momentum with respect to the body. Sketch the flow of momentum through body and rope. How would you introduce forces in this case? What is their relationship to the fluxes and sources expressed as vector quantities?

4. A rope with a given (constant) mass per length is hanging from a hook. Express the equation of balance of momentum for small segments of the rope and derive the appropriate differential equation for the continuous case. Then determine the momentum current density in the rope as a function of position. How does this quantity relate to the mechanical stress in the rope?

5. Consider a long bar falling in an inhomogeneous gravitational field increasing linearly downward (Section 3.3.2). The body is assumed to be rigid. (a) Calculate the acceleration of the body with the help of the equation of motion of the entire body. (b) Compute the momentum current density through the body as a function of position in the body. (Hint: set up the equation of balance of momentum for the spatially continuous case).

6. Two gliders with magnets move toward each other on an air track. When they move closer, they are repelled. Friction is noticeable since the air stream is relatively weak. In the following diagrams, Fig. P.6, you can see the distance between the gliders and their velocities. Data: Mass of glider 1: 0.868 kg; mass of glider 2: 0.618 kg. (a) Which of the velocity functions belongs to the smaller of the gliders? a or b? Why? (b) Assume a constitutive law of the form $I_{pR} = \mu I_{pN}$ for the momentum transfer due to friction with a coefficient of dynamic friction μ and the normal force I_{pN} (i.e., friction is assumed to be constant). Determine the coefficient of friction. (c) Determine the momentum current through the magnetic field at the time of the shortest distance between the gliders. (d) If you look at a single magnet, what is the type of momentum transfer with respect to the material?

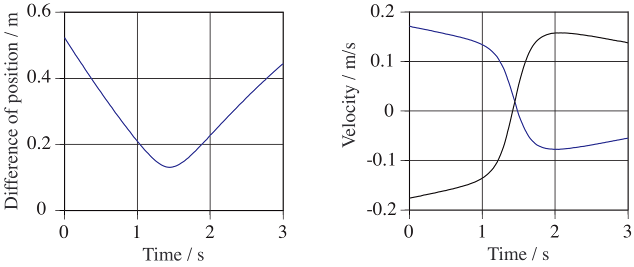

Figure P.6

7. A tennis ball rests atop a soccer ball. Both are dropped together. In the diagram, Fig. P.7, you see the data of the positions of the centers of the two bodies as functions of time. Mass of the soccer ball: 442 g. Mass of the tennis ball: 56 g. Neglect air resistance in your analysis. (a) Construct the free body diagrams of the balls (separately) for the duration of the impact with the floor. Identify all momentum transfers with respect to the bodies. We assume that the tennis ball touches the soccer ball during the impact with the floor. (b) Determine the speeds of the bodies shortly before and shortly after the impact with the floor. Determine the momenta of the bodies. (c) How much momentum was exchanged with the ground? If the collision lasts for about 4 ms, what was the average momentum current? (d) How much energy was dissipated? (e) If the processes were dissipationless, would the momentum exchanged with the floor be larger, equal, or less than for the real case?

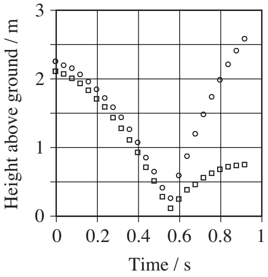

Figure P.7

8. A buffer for train cars is designed and simulated with the help of a model. A train car having a mass of 10 tons moves on a horizontal track and hits a hard obstacle at a speed of 5 m/s. The elastic properties of the buffer are modeled as a linear spring having a length of 0.50 m. Internal friction is modeled as a constant force having the same value for compression and expansion. (a) If the car hits the obstacle at 5 m/s, the spring may not be compressed more than its length, even if we neglect internal friction. What is the minimum value of the spring constant? (b) Again, neglect internal friction in the spring. What is the duration of the collision? (c) The diagram shows the simulated acceleration of the car. Explain the result formally. (Friction due to the rails and air resistance are neglected.) Determine the value of the damping force.

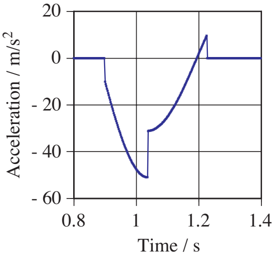

Figure P.8

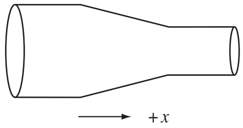

Figure P.9

9. A liquid having a density of 920 kg/m^3 is flowing through a pipe whose diameter decreases from 3.0 cm to 1.5 cm (Fig. P.9). The speed of flow at the smaller exit is 4.82 m/s. (a) Compute the convective momentum fluxes at the inlet and the outlet. (b) The pressure of the fluid at the inlet is 1.10 bar. Calculate the conductive momentum flux at the entrance. Compare the magnitude of the convective and the conductive fluxes.

10. In the previous problem compute the force which holds the pipe in place. The pressure of the surrounding air is 1.0 bar. Take the flow through the pipe to be ideal.

11. A rocket is moving through space far from any gravitational fields and at constant speed v_0 with respect to an observer. The engines are ignited so that the flux of mass out of the rocket is constant, and the speed of the gases is v_g with respect to the engines. (a) Formulate the equation of balance of momentum for the rocket with respect to the observer. (b) Solve the equation of motion.

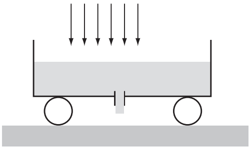

Figure P.12

12. An open car moves underneath a vertically falling current of water (Fig. P.12). At the same time, the car loses water through a hole at the bottom at the same rate at which it picks up water. Set up the equation of motion for the car and determine its speed as a function of time. Assume friction to be negligible.

13. A Scout X1 rocket of NASA with a total mass of 16 tons stands upon the launch pad. After ignition, 220 kg gas per second flows out of the engine at a speed of 2100 m/s. Information: Disregard air resistance and take a value of 10 N/kg for the strength of the gravitational field. (a) Write the law of balance of momentum for the rocket as a system. Why is the rate of change of momentum *not* equal to the mass times acceleration? (b) What is the rocket's acceleration right at the beginning? What is the acceleration after 40 seconds of engine firing? (c) What speed does the rocket reach after the 40 seconds of firing the engines?

14. A flat plate with a surface area of 0.50 m^2 is pulled horizontally over another plate with a film of oil between them. The film has a thickness of 4.0 mm. To move the plate at constant speed of 1.0 m/s, one has to pull with a force of 25 N. What is the viscosity of the oil?

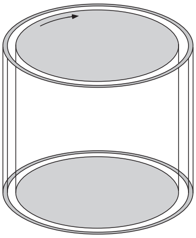

Figure P.15

15. A fluid is confined between the walls of two concentric cylinders (Fig. P.15). The gap between the cylinders is very narrow. The inner cylinder can be rotated, and the torque upon it and the angular velocity can be measured. Determine the viscosity of the fluid.

16. Show that if you use momentum as the fundamental quantity, a (linear) spring is an inductor. Determine its inductance. Show that a body hanging from the spring has the property of a capacitor. Now determine the frequency of oscillation from the capacitance and the inductance of the system.

17. Set up the equation of motion of a body hanging from a (linear) spring. Solve it and show that you get the same expression for the frequency of oscillation as that found in the previous problem.

18. Use the expression for the power of a process for calculating (a) the energy required for lifting a body of mass m a certain distance h at the surface of the earth, and (b) the energy released from an electric field when an electron moves through a given voltage U in the field.

19. A car moving horizontally at a constant speed of 120 km/h is using 8.0 liters of gasoline for a distance of 100 km. The mechanical efficiency of the engine is 0.20. Draw a process diagram for the car as the system, depicting energy carriers, energy currents, and power. How large is the magnitude of the sum of all resistive forces acting upon the body? Repeat the flow diagram with the engine as the system.

20. A linear spring is attached to a wall on one side. As it is stretched, determine all energy fluxes with respect to the spring. Calculate the change of the energy content of the spring as a function of the stretching.

PART II

THERMAL AND CHEMICAL PROCESSES

CHAPTER 4

STORAGE, FLOW, AND PRODUCTION OF HEAT

Thermodynamics is the science of heat and hotness, of how bodies and other physical systems respond to heat, and of how heat can be used to drive other processes. In this chapter, I will introduce the fundamental quantities and concepts of thermodynamics and create dynamical models of some interesting phenomena. I shall justify the generic laws of thermal physics which we are going to use throughout this book. Constitutive laws will be introduced on an informal basis when needed for getting answers to some special problems. They will be treated in great detail in the following chapters.

I will take a practical approach to thermal processes by creating dynamical models of the heating and cooling of simple materials, the storage of heat in such materials, the flow of heat through walls, production of heat, and the operation of heat pumps and heat engines. This development will be guided by the balance of quantities of heat, by the interpretation of temperature differences as the thermal driving force, and by Sadi Carnot's comparison of waterfalls and heat engines to motivate the relation between heat, hotness, and power. First however, let us take a look at what kinds of images and concepts can be formed about heat and hotness from our everyday knowledge of thermal processes.

4.1 THERMAL PHENOMENA, CONCEPTS, AND IMAGES

Thermal phenomena are part of our everyday experience. They allow us to conceive of the quantities which are necessary for a theory of thermal physics. Nature tells us where to begin and what to look for. On the basis of experience, we construct the concepts which we do not derive from anything else, i.e., those which are truly fundamental. I shall take these to be *hotness*, *heat*, and *energy*. We intuitively know the first two of these quantities, even though our knowledge is not precise in any scientific sense. We have become familiar with energy through our study of other parts of physics. By weaving the elements into a theory of thermal processes, and by comparing the predictions of the theory with new phenomena, we will find out whether our ideas are correct.

Assuming that you probably have had at least a moderate exposure to thermal physics, you might find this section the most demanding of all, even though there will not be a single equation to set up or to solve. It is imperative that you see very clearly how common sense reasoning and analogies can be used to understand the meaning of heat and hotness before we go on with the formal story.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_5,

4.1.1 Some Phenomena and Word Models

This subsection serves a simple purpose: To create word models of some basic thermal phenomena. These models which are created almost effortlessly on the basis of conventional language will demonstrate everyday conceptualizations of processes involving heat and hotness. The result is a language which could just as easily be used to speak about fluid and electric processes. There is a quantity of heat residing in bodies, making them warm, letting them expand or melting them. It is capable of flowing into or out of these bodies; it can be produced by fire, electrically, or by rubbing, and it can be used to drive engines. Temperature differences make all these things happen.

Two bodies of water in thermal contact. Water is poured into two identical compartments of a container separated by a thin metal wall. In one of the compartments there is hot water, in the other one the water is cold. The container is well insulated and covered by a styrofoam lid. The bodies of water are stirred continuously, so there is a uniform temperature for each body. It is found that the temperature of the hot water goes down whereas the temperature of the cold water rises. This continues until both temperatures are the same and pretty much equal to the average initial temperatures.

Temperatures equilibrate for bodies made of different materials and sizes as well. Data has been taken for a block of cold copper in hot water (Fig. 4.1). In general, the final temperature lies somewhere between the initial values for the bodies in thermal contact.

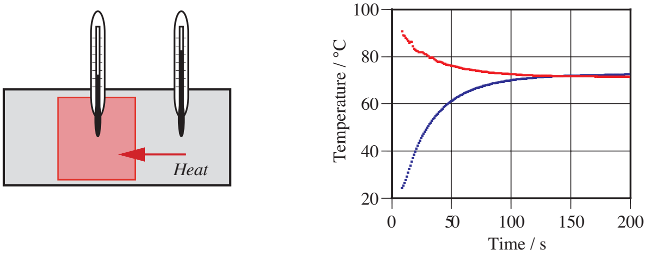

Figure 4.1: A hot body of water in thermal contact with a cold copper cylinder inside a well insulated container (left). The temperatures adjust until they have become equal (right).

Interpretation. For a body of water to get colder, it has to lose heat, for it to get warmer, it must gain heat (Fig. 4.1, right). We say that heat flows from the hotter body of water to the colder one as long as there is a temperature difference. We interpret temperature differences as the *driving force for the flow of heat* and *temperature as the thermal level* because the behavior of the temperatures resembles that of water levels in communicating tanks, or of voltages of capacitors connected by a resistor (Fig. 1.1 or Fig. 1.3). The example in Fig. 4.1 demonstrates that thermal levels become equal, not quantities of heat residing in the bodies making them warm. Put differently, temperature does not measure quantities of heat, it tells us *how warm* a material is.

The water in the container would lose heat to the cool environment and the temperatures would drop further were it not for the insulation. Styrofoam insulation makes it difficult for heat to flow out of warm bodies.

Thermocouples, resistors, and air thermometers. Different devices and materials can be used to measure temperature. Basically, whenever we have a process or a material property dependent upon temperature or temperature differences, these can be exploited to build thermometers. Simple combinations of two metals—so-called thermocouples, which are actually thermoelectric generators (see below in Fig. 4.11)—can be used to measure temperature differences. The resistance of electric resistors commonly depends upon temperature (Fig. 4.2, left), so we can build resistive thermometers. An important type of thermometer is made from a simple gas such as air whose pressure depends upon its temperature (Fig. 4.2, right).

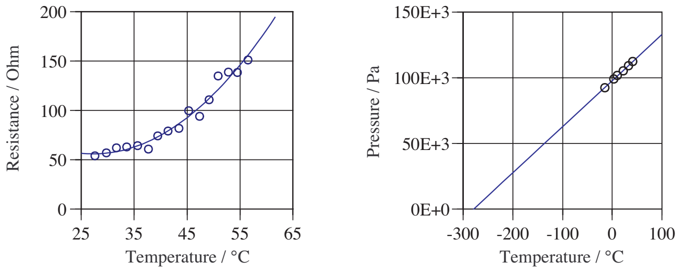

Figure 4.2: Resistance of a resistor as a function of temperature (left), and pressure of air at constant volume as a function of temperature (right; the relation is extrapolated backwards to zero pressure).

Interpretation. Using the gas thermometer, the pressure of a dilute gas such as air at standard conditions is measured at constant volume. It is found that—if the temperature is not too low—the pressure is a linear function of temperature. This relation is extrapolated backwards to a pressure of zero. The same temperature is found for zero pressure independent of the type of substance that is in a gaseous state; the result is a temperature of – 273°C, therefore it is assumed that this constitutes a special point. Since lower temperatures than the zero point of the air thermometer have never been found in any experiment, it is believed that it represents the lowest possible temperature that can be attained. The *Kelvin temperature scale* uses the zero point of the air thermometer as its starting point.

Compressing air. Air can be compressed quickly in a bicycle pump. If we do this repeatedly, the end of the pump becomes quite warm. We can perform the same process in a cylinder with a piston and put a small piece of tinder in the cylinder. Already after a single quick stroke the tinder is observed to ignite in a flash.

Interpretation. The fact that the tinder ignites tells us that the air has become very hot. This explains why a bicycle pump becomes hot after a few strokes. Heat flows from the hot air through the pump casing into the surroundings.

Why does the temperature of the air rise so dramatically as the result of a quick, strong stroke? After all, there is no fire to heat the air, heat cannot flow from the surroundings into the air (the air is hotter than the surroundings!). So we do not add heat from outside. There could be friction in the air, and indeed there is, but its effect is very small (this is explained by noting that the compressed air is almost ideally elastic, the volume would be restored if we just let the piston move out again). Since we do not add heat, and since heat is not produced, the quantity of heat of the air stays constant. The temperature of the air rises because its heat is compressed into a much smaller space; the heat of the air is lifted to a higher level (Fig. 4.3).

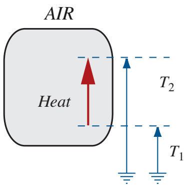

Figure 4.3: Process diagram of compression of air without heating or cooling. The temperature of the air rises. Figuratively speaking, the heat of the air is lifted to a higher level.

This example demonstrates very convincingly that temperature and heat cannot be the same quantity—remember, we already concluded this by observing that temperature, not heat, equilibrates. When air is compressed quickly, the quantity of heat stays constant while temperature rises dramatically.

Cooling and heating water in a can. Hot water is poured into a thin aluminum can.

The water is stirred continuously with the help of a magnetic stirrer, and its temperature is recorded (Fig. 4.4, top left). The temperature drops quickly at first, and more slowly later on. Finally, it reaches a constant value; interestingly this value is higher than the temperature of the environment.

If very cold water in a drinking can is left standing in a warm room, its temperature rises quickly at first, and then more slowly (Fig. 4.4, top right). In the case presented here, the drinking bottle is inside an insulating jacket, and the water is stirred during the observation. Note that the temperature of the water rises above that of the room.

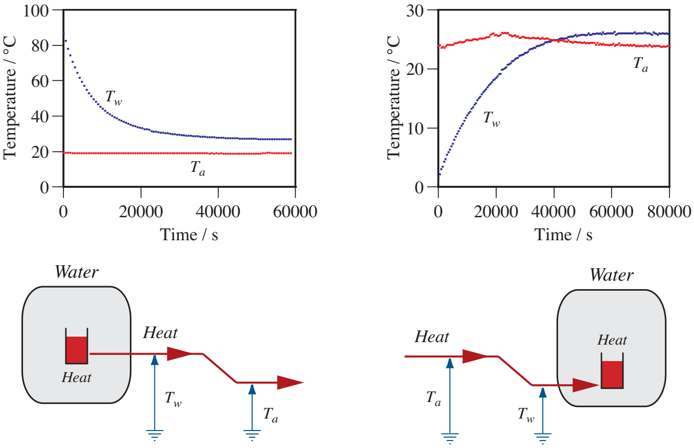

Figure 4.4: Top left: Temperature of hot water left standing in a thin-walled aluminum can. The final temperature is above the temperature of the environment (here about 20°C). Top right: Temperature of cold water left standing in an insulated drinking bottle. The final temperature is above the temperature of the environment (the curve that starts at about 23°C). Bottom: Process diagram for heat flowing into or out of a storage element. A temperature difference drives the flow.

Interpretation. Hot water loses heat to the environment through the wall of its container (Fig. 4.4, bottom left). The difference of temperatures between the water and the environment serves as the *driving force* for the flow of heat. If the driving force is greater, the loss of heat is greater, letting the temperature go down faster. This explains the shape of the measured curve (see also Fig. 4.1). The magnetic stirrer used to stir the water produces some heat. That is why the temperature of the water settles above the temperature of the environment: In the end, the heat produced by the stirrer must leave the container, so there needs to be a temperature difference.

If the water is colder than the environment, heat will flow from the environment into the cold water (Fig. 4.4, bottom right). Again, if the temperature difference is high, the flow will be strong, the temperature of the water will change fast. Since heat is generated by the stirrer, the final temperature of the water will be above that of the environment (Fig. 4.4, top right).

Heat flows through a metal bar. A section of a copper bar is inserted into water in a glass. The rod is heated by a candle at the other end (Fig. 4.5, left). Over time, the temperature of the water rises. In a somewhat more sophisticated experiment, one end of a long, thin copper bar is stuck in ice water, and the other end is heated electrically. The bar is not insulated from the surrounding air. The temperature of the metal is measured at eight points along its length (Fig. 4.5, right). Temperatures first drop a little. Soon after the heater is turned on, the temperatures rise. The parts of the copper bar near the end that is heated become hot first. For the other points there is a more or less prolonged delay in response.

Interpretation. Heat is produced by the candle and transferred through the copper rod into the water. The flame is very hot, the copper rod is pretty hot at the heated end and cooler at the end stuck in the water; the water is cooler still. Heat flows from hot bodies to colder ones. Heat accumulates in the water and as a result, the temperature rises.

In the second case, some heat slowly flows out of the copper bar (which is at room temperature) into the ice water. If heat has to flow from points farther away, those parts get colder more slowly. When the electric heater is turned on, heat is produced (see Fig. 4.9) and it travels through the length of the bar toward the end stuck in the water. The parts of the bar closer to the heater receive the heat first, so their temperature rises most quickly. The rise of temperature is delayed in the sections of the bar farther away from the heated end. As time progresses, a fixed temperature gradient from hot to cold is established.

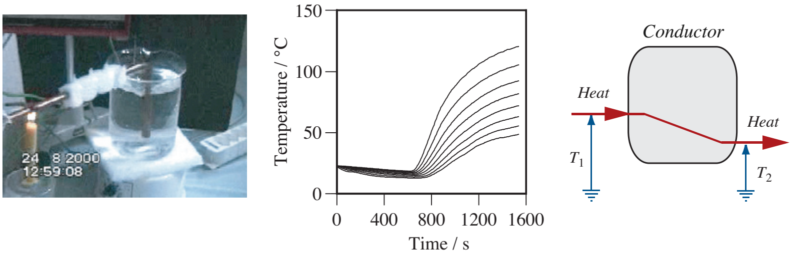

Figure 4.5: Left: A candle heats water indirectly. A copper rod transfers the heat produced by the candle to the water. Center: Temperatures of a long copper bar at different points as functions of time. First, the bar is at room temperature. One end is placed in cold water. Starting at $t = 700$ s, the other end is heated electrically. Right: Process diagram of heat flow.

The process of migration of heat through a material is called *conduction*. It is analogous to the conduction of electricity in metals. As the curves in Fig. 4.5 suggest, it is also similar to the flow of water through a chain of tanks, or the transport of charge through a chain of *RC* systems (Fig. 1.28).

Melting ice and freezing water. Ice placed in a warm environment melts. Alternatively, we can actively heat ice in a test tube placed in warm water and monitor the temperature of the mixture of ice and water forming from the ice, and of the water bath (Fig. 4.6). It is found that the temperature of a cold block of ice first rises to 0°C. Then the ice-water mixture in the test tube stays at a constant 0°C until all the ice has melted. Only then, upon further heating, does the temperature of the water in the test tube rise as expected. The temperature of the water bath decreases all the time.

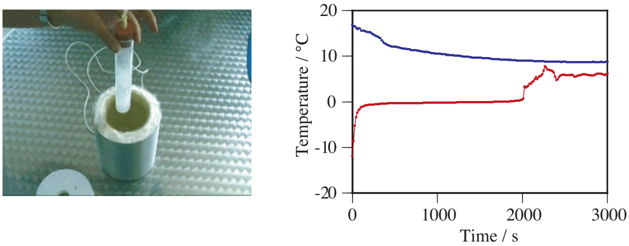

Figure 4.6: A test tube filled with cold ice is placed in water, everything is in a well-sealed glass container. Temperatures of the water bath (upper curve) and of the ice-water mixture in the test tube (lower curve) are recorded.

When water is placed in a cold environment (considerably colder than 0°C), the reverse happens. The temperature of the water drops to 0°C. Now ice starts to form and the temperature of the freezing substance stays constant at 0°C. Finally, when there is only ice, the temperature continues to sink below the freezing point.

Interpretation. Obviously, heat is needed to melt ice. First, heat coming from the warm water raises the temperature of the cold ice to 0°C. Then the temperature of the substance in the test tube (Fig. 4.6) stays constant for quite a while. During this phase of constant temperature, ice transforms into water. Since the mixture is colder than the surrounding water, heat continues to flow into the melting mixture. In this case, heat does not raise the temperature of the material. Rather, it leads to the transformation of ice to water.

Again we have an example that demonstrates very clearly that heat and temperature are totally different concepts. While the temperature stays constant, the quantity of heat of the substance in the test tubes increases.

Vaporization of water. Water is placed in an open but otherwise well insulated can on top of a scale. The water is heated with an immersion heater. At a temperature of almost 100°C, it starts to boil. The power of the heater is kept constant. Temperature and mass of the water are recorded. We find that the temperature stays constant during vaporization, whereas the mass of the water decreases continually (see Fig. 4.7).

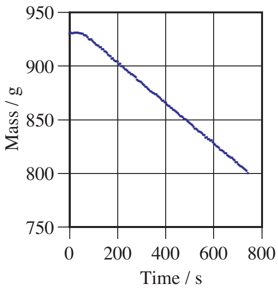

Figure 4.7: Water is vaporized in a can on top of a scale. The mass of the water is recorded as a function of time. (The temperature stays constant during vaporization.)

Interpretation. Again, we have a phase change that requires heat while the temperature of the substances undergoing the change (water and steam) stays constant. Heat is produced at a constant rate by the immersion heater. Since the mass of the water decreases linearly, we conclude that equal amounts of heat produce equal quantities of steam.

A Peltier cooler. Two bodies of water inside a well insulated tank are separated by a so-called Peltier device (Fig. 4.8, left; see also Fig. 4.11, left). This is a particular type of thermoelectric device. It can be hooked up to an electric power supply. If we set up a voltage across the device, we observe that one of the bodies of water becomes colder whereas the other one gets warmer (see the diagram in Fig. 4.8, right). Overall, the system gets warmer if the tank is sealed.

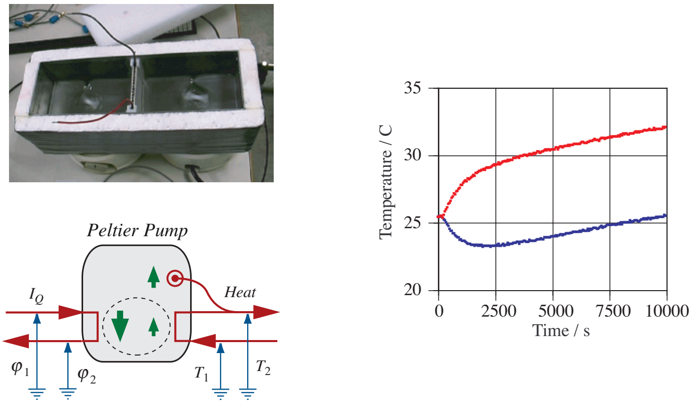

Figure 4.8: Two bodies of water inside an insulated tank are separated by a Peltier device (top left, see also Fig. 4.11). When operated, the Peltier device cools one body of water and heats the other. Bottom left: Process diagram of Peltier heat pump. Electric charge flowing from higher to lower electric potential releases energy which is used to drive the pump and to produce more heat.

Interpretation. The body of water getting warmer is gaining heat, the other one is losing heat. It makes sense to assume that the heat added to the former is taken from the latter. Since heat goes from a cold to a hot body, it does not flow by itself as in conduction (Fig. 4.5). Heat is said to be *pumped* by the thermoelectric device. Like any other pump, this one also needs energy to do its job (Fig. 4.8, bottom left).

The Peltier device also produces heat; the material through which the electric charge flows has a certain resistance and heat is produced as it is in any electric resistor. As a consequence, the heat of the two bodies of water taken together increases, and the average temperature rises.

A thermoelectric device is a material that conducts electricity (electric charge) and heat. There are no moving parts, and no fluids transporting heat. Therefore, it appears that in a thermoelectric device electric charge can transport heat.

Immersion heaters. One of the simplest thermal devices is an electric heater to heat water. If it is immersed in water, and as long as it is operated, the water either gets warmer or boils away (Fig. 4.9, left).

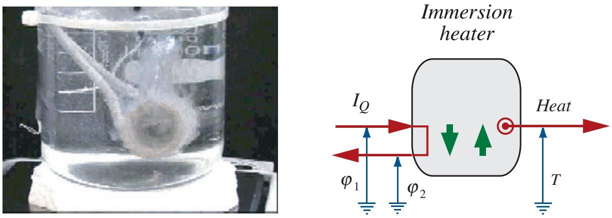

Figure 4.9: Left: An immersion heater heats water which starts to boil. It provides heat to the liquid. Right: Process diagram of an electric heater. Note the difference to the diagram of a Peltier device (Fig. 4.8): Heat does not flow in from a cold place.

Interpretation. We know from the foregoing discussions, that water needs heat if it is to get warmer or boil. Obviously, the heat must be supplied by the electric immersion heater. Since the heater can be operated almost indefinitely, it cannot supply the heat from its own store—there simply cannot be enough of it in the wire. We conclude that an electric heater produces heat, a process we have seen to be operating in many other cases as well. The process diagram of the heater (Fig. 4.9, right) explains how this is to be understood. Energy is released in the electric process and made available to a follow up process which is the production of heat. Heat is produced out of nothing, but not by itself—there has to be a process providing energy.

A Stirling engine. A Stirling engine is a classical heat engine. The engine is heated from outside (any type of heating will do: a fire, electrical heating, heating by concentrated solar radiation, etc.), and cold water is passed through it to cool the engine (the water leaving the engine is warmer than the water entering). When operated like this, the engine can drive mechanical processes (Fig. 4.10, left). The "working fluid" is air or some other simple gas. When the flow of cooling water is reduced, say, by a factor of two, the temperature difference of the fluid also changes by a factor of two, and the engine works somewhat less efficiently.

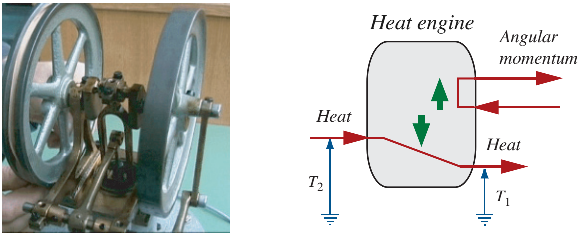

Figure 4.10: Left: The mechanical part of a Stirling engine. When the engine is heated and cooled, the wheels drive a mechanical process. Right: Process diagram: Heat falls from high to low temperature, thereby driving a rotational process.

Interpretation. The following interpretation is motivated by Sadi Carnot's explanation from his famous book *The Motive Power of Heat* (1824).[1] Heat (he also called it caloric) falls from the high temperature of the furnace to the low temperature of the cooler. Doing so it releases energy used for driving the mechanical process of the engine. All the heat supplied by the furnace has to leave through the cooler into the environment. This explains why the temperature of the cooling water rises more if its flow through the engine is smaller. And it explains why the engine is less efficient: The temperature drop from the furnace to the cooling water is smaller.

Note that the process diagram on the right in Fig. 4.10 is essentially the reverse of the one for the Peltier heat pump in Fig. 4.8. Stirling engines, by the way, make great heat pumps or refrigerators. They just have to be operated in reverse, i.e., they have to be driven mechanically.

Thermoelectric generator. A Peltier device can be run in reverse in which case it functions as a heat engine—in this case as an electric generator. Placed between a hot and a cold body of water, a voltage develops across the terminals of the device. If we attach a load to the device, it drives an electric process whose power can be measured from voltage and electric current (Fig. 4.11). Compared to mechanical heat engines operating between similar temperatures, the efficiency of the Peltier device is quite low.

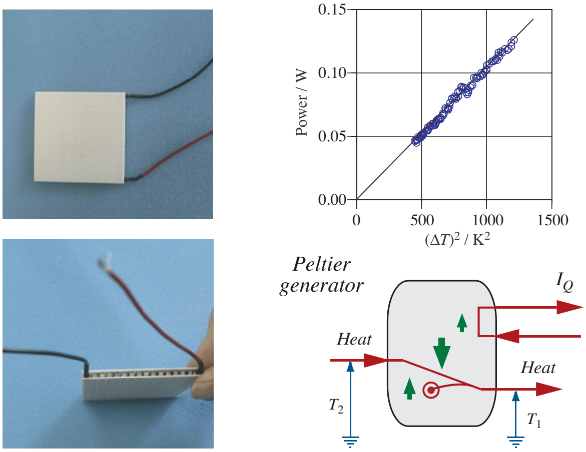

Figure 4.11: Photographs of a Peltier device. The electric power of a thermoelectric generator (a Peltier device between two heat reservoirs at different temperatures) is proportional to the square of the temperature difference. Bottom right: Process diagram of the Peltier generator.

Interpretation. The process diagram explains the operation of the Peltier heat engine. Note that it is fundamentally similar to the one for the Sterling engine (Fig. 4.10). Heat falling from higher to lower levels releases energy which is used to drive the desired process, i.e., the flow of electric charge from lower to higher potentials. Here, however, it is quite clear that only a fraction of the energy released is used to drive electricity. Much of it is used to produce more heat; this is a consequence of the particular structure of the thermoelectric device.

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[1] S. Carnot (1824).

The measured power is proportional to the square of the temperature difference between the hot and the cold water (Fig. 4.11). This is analogous to what we know of the power of an electric load resistor which is proportional to the square of the voltage. Assume the energy released by heat to be proportional to the temperature difference. If the flow of heat is also proportional to the temperature difference, the resulting dependence of power on the temperature difference is what we observe in Fig. 4.11.

Reversing the operation of an electric water pump. In an electric pump, the electric process drives the hydraulic one (Fig. 4.12, left). At the same time, the device becomes warm: heat is generated. The system can be reversed. A system of turbine and generator reverses the electric and hydraulic processes (Fig. 4.12, right). When it is running, it becomes warm: heat is generated.

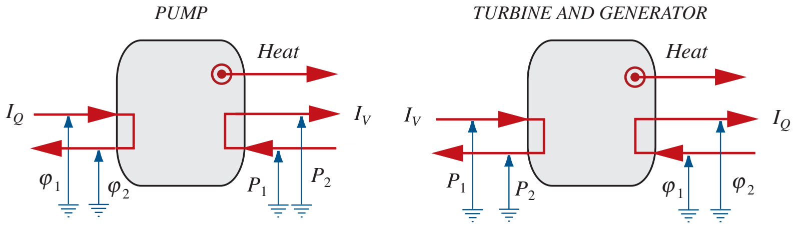

Figure 4.12: Process diagram of an electrically driven pump (left) and its reverse, a system of turbine and generator. Both systems produce heat. The production of heat cannot be reversed—this is what we mean by irreversibility.

Interpretation. Physical processes can be reversed, with one exception. This is the production of heat. If we had to reverse all the processes of a heat producing system, we would have to destroy heat. This does not happen. Instead, heat is again produced. We conclude that heat is a quantity that can be produced but not destroyed.

QUESTIONS

1. Why does the phenomenon shown in Fig. 4.1 show that temperatures rather than quantities of heat equilibrate when bodies are in thermal contact?
2. What does temperature measure?
3. In Fig. 4.1, the temperature reached by copper and water (diagram on the right) is above the average of the initial temperatures of the two bodies. Why is this so? How does this compare with similar phenomena in hydraulics or electricity?
4. What does the example of conduction of heat through a metal bar (Fig. 4.5) tell us about the role of temperature and the flow of heat?
5. Does heat always make a body warmer? Do we always need heat to make a substance warmer?
6. Why do the processes of melting (or of vaporization) and of compression of air demonstrate clearly that heat and temperature cannot be the same quantity?
7. To make water warmer, we need heat. Where can the heat come from? Does it matter for the water where the heat comes from?
8. What is the role of energy in the Peltier heat pump of Fig. 4.8? Why does the production of heat make the device less efficient?
9. Why does measuring the power of a Peltier generator (Fig. 4.11) suggest that the power of heat is proportional to the temperature difference through which heat flows?
10. What are some means of producing heat?
11. What kinds of processes can be reversed? Which ones cannot?

4.1.2 Hotness and Temperature

In this and the following subsections I am going to summarize the experience from the word models of thermal phenomena presented above and provide some additional background on the choice of primitive quantities—heat, hotness, and the power of thermal processes—to build the dynamical theory of heat for this book.

One of our most direct experiences with thermal phenomena is the observation that objects feel hot, warm, or cold. We have a sensation which allows us to place objects in a sequence which we label cold, cool, warm, hot, or very hot. From the *sensation of hotness* we abstract a primitive quantity which we call *hotness*. A primitive quantity is one which we do not derive in terms of other more fundamental quantities.

The concept of hotness goes back to E. Mach.[2] He considered it to be natural and fundamental, like so many other concepts upon which we build the foundations of science. Imagine it to be something like a line on which we organize bodies according to how hot they are, just like beads on a string. Mach wrote:[3]

> Among the sensations by which, through the conditions that excite them, we perceive the bodies around us, the sensations of hotness form a special sequence (cold, cool, tepid, warm, hot) or a special class of mutually related elements … . The essence of this physical behavior connected with the characteristic of sensations of hotness (the totality of these reactions) we call its hotness … . The sensations of hotness, like thermoscopic volumes, form a simple series, a simple continuous manifold … .

The sensation of hotness might serve as a first measure of the physical quantity, albeit not a very reliable one. Naturally, we would like to learn how to determine hotnesses reliably. There are measures of hotness which are more useful than our senses, such as the volumes of bodies which change with the hotness. We can build simple devices to tell how hot an object is. These devices are *thermometers*, with which we measure temperatures. Now, what does *temperature* have to do with the concept of hotness? There is a simple image which explains the relationship. Temperature is like a coordinate on the hotness manifold; it is a numerical indicator of hotness. This, by the way, lets us expect that there may be many possible *temperature scales*, just as there are many possible ways of introducing coordinates along a line. According to Mach:[4]

> The temperature is … nothing else than the characterization, the mark of the hotness by a number. This temperature number has simply the property of an inventory entry, through which this same hotness can be recognized again and if necessary sought out and reproduced … . This temperature number makes it possible to recognize at the same time the order in which the indicated hotnesses follow one another and to recognize between which other hotnesses a given hotness lies.

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[2] E. Mach (1923) analyzed the development and the logical foundations of thermal physics. An interesting passage in his book compares the potentials associated with different phenomena (velocity for translational motion, electric and gravitational potentials, and temperature).

[3] E. Mach (1923), p. 43. With the exception of the choice of a term the translation is from C. Truesdell (1979).

[4] E. Mach (1923), p. 44. In recent years, efforts have been made to base the foundations of thermodynamics upon the hotness as a primitive concept (Truesdell, 1979, 1984; Pitteri, 1982).

There is an interesting and important feature of hotness: it has a lower limit. Experience tells us that this should be the case. Bodies cannot get colder than "really cold." We have never found bodies with a hotness below a certain level, which we call the *absolute zero of hotness*. Put differently, we can say that hotnesses are strictly positive. In fact, the point of absolute zero cannot be reached; it only can be approached. This has been done in experiments to an ever increasing degree. Nowadays, temperatures within a small fraction of one unit (1 Kelvin) from absolute zero can be reproduced.

4.1.3 Heat and Hotness

So far we have heat and hotness as the two primitive concepts for building a theory of thermodynamics. Still, many people do not consciously distinguish between the sensation of hotness, and amounts of heat. The term *heat* is often used in the sense of something being hot. Therefore it is important to stress again the difference between these concepts, and then say positively what we believe the properties of heat to be.

Heat and Hotness. Simple observations tell us that the two quantities cannot be the same. Take an amount of water. We assume that it contains a certain amount of heat. Divide the water into two equal volumes. What can you say about the heat contained in each part, and the sensation of hotness of the parts? Experience tells us that their hotnesses are equal and the same as that of the original body of water. However, the heat content has been divided equally among the parts. Therefore the sensation of hotness and amount of heat are clearly two different things. Hotness is called the *intensive* thermal quantity while heat is the *extensive* one.

Two phenomena demonstrate beyond any doubt that heating is not just another word for change of hotness (in which case there would not be any need for a new quantity!). The first is the melting of ice. When ice is heated, it melts, but its hotness does not change as long as there is a mixture of ice and water. The second one is the fast compression of air without heating or cooling (without adding or withdrawing any heat). The temperature of the air rises greatly whereas the heat of the gas is not changed.

Temperature differences as the thermal driving force. Consider the following example that serves to illuminate the role of hotness even further. Place two bodies at different temperatures in thermal contact and monitor their temperatures. We know what will happen. In the course of time the hotter body will cool down while the cooler one must heat up. Experience tells us that this continues as long as the temperatures are different. Finally, after some time, the hotnesses have become equal and the process stops (Fig. 4.1). Another interpretation of this phenomenon is to say that heat flows by itself from the hotter to the cooler body as long as there is a difference of temperatures.

We have seen analogous processes in other fields of physics (Table 4.1). Two containers filled with water and connected by a hose, or two charged bodies connected by a wire, behave similarly. In those cases we speak of the flow of a certain physical quantity as a consequence of a driving force. We have defined driving forces as the difference of potentials between the physical systems. If we take these phenomena as a guide, we can interpret a difference of temperatures as the *thermal driving force* and hotness as the *thermal potential*. In graphic language, hotness takes the role of the thermal level.

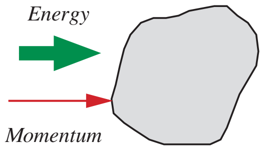
The driving force determines the type of process taking place. In this sense we say that a thermal process is one in which heat flows due to a difference of temperatures. Note that not every mode of heat flow is a thermal phenomenon according to this definition. Witness the following example: you can carry around a bucket of hot water, which means that heat is being transported. But certainly this is not a thermal process. Hotness plays a central role in what we call a thermal phenomenon, and we may not forget the qualifier given in the definition above.

Table 4.1: Comparison of some processes

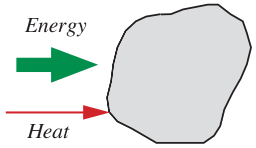
	Quantity	**Potential**
Water containers joined by a hose	Water	Water level
Charged spheres in contact	Electric charge	Electric potential
Bodies at different temperatures	Heat	Hotness

4.1.4 The Properties of Heat

There are two important points to consider at the beginning of any discussion concerning the nature of heat. First, we would like to know what is responsible for making a stone warm or for melting a block of ice. Second, we have to recognize the difference between a moving body, a charged sphere, and a hot stone, as well as how this difference can be expressed in a theory of physics.



Accelerating



Heating

Figure 4.13: Two processes compared. In the first we accelerate a stone. In terms of physics, we say that momentum is added to the body, which makes it move faster. We know that energy is added to the stone at the same time. In the second case, the stone is heated rather than accelerated. The difference between the situations is that now we add heat rather than momentum. Heat is responsible for making the stone warmer.

It is quite clear that *heat* makes a stone warm and melts an ice cube. We put more heat into a body such as a stone to make it warmer; taking heat out of the stone will make it cool down. If we put ice in a warm place, heat will enter the body and make it melt. *Heat* is the perfect quantity for describing what is happening in these situations.

What heat is not. The second question goes to the core of what heat is not. First try and answer this question: What do the moving, charged, and hot body have in common? Again the answer is quite clear this time for those who have studied physics. In all three situations the body has received energy (Fig. 4.13). In each case, the system contains more energy than if the body were not moving, if it were not charged, or if it were not hot. Seen from the viewpoint of energy, the situations are all the same, and we should rather ask about how a stone which is moving differs from a stone which is hot. We might learn more about how nature works from the answer to this question.

We could say that the difference lies simply in the fact that the moving body has received an amount of motion while in the case of the hot body we have added some heat (Fig. 4.13). We have learned that amounts of motion are measured in terms of momentum. Changing the motion of a body requires that we change its momentum. True, we also change the energy of the body at the same time, but knowing that the energy of a system can be different for many different reasons, we take momentum as the quantity which tells us why the body is moving rather than becoming hot.

Applying this argument to the hot body, we have to conclude that the stone is hot not because it contains energy but because it has more heat than if it were colder. A stone gets hot and an ice cube melts because of heat. Even though energy accompanies all processes, heating included, it cannot distinguish between them. The point is this: *heat is not energy*.

The laws of physics help us to assure ourselves of this point. You know that energy is a different measure of gravity or inertia (Chapter 3). Increasing the energy of a system means increasing its mass. It does not mean that the body has necessarily become faster, hotter, or both; it might just as well have become electrically charged. Energy, i.e., mass, cannot be used to distinguish between different processes. We absolutely need other quantities such as momentum or charge, if we wish to state what has happened to a body. Applied to thermal processes this means that if heat is the quantity responsible for warming a stone or melting ice, rather than making the bodies heavier, then heat cannot be energy.[5]

Heating and cooling: Transport of heat. Clearly, the hotness of objects can change. The sand at the beach is hot at noon, and cool at night. We can get hot water for coffee by heating it. Ice is produced by cooling water.

Therefore, there is more to thermal phenomena than just the hotness. We definitely need a means for changing this quantity. Again, on the basis of every-day experience, we can introduce the notion of *heating* (or cooling). We can heat bodies slowly or quickly; hence we often speak of the rate of heating. However, we have used the word *heating* already in the sense of a rate, namely the *rate of transfer of heat* to a body. *Cooling* stands for the rate of transfer of heat out of a body (Fig. 4.14). We clearly have to distinguish between heating and cooling on the one hand, and getting warmer or getting colder on the other.

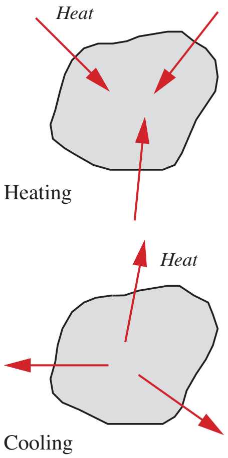


Figure 4.14: Heating and cooling. By *heating* we mean the flow of heat into a body. In the case of *cooling*, heat flows out of the body. We assume that heat is a quantity which can flow. Also, we believe that heat can be stored in bodies.

Obviously, heat can be transported. Heat from the sun arrives at the Earth, where it is distributed in the atmosphere before it is radiated back into space. Heat flows out of the depths of the Earth to the surface. A metal bar which is heated at one end also gets hotter at the other end, which demonstrates that heat becomes distributed throughout the body. Large amounts of heat are transported from the Gulf of Mexico to Europe with the help of the Gulf Stream. Central heating systems transport heat from the burner to the radiators from where the heat flows into rooms. There are many aspects of life which are influenced by the flow, transport, or distribution of heat. We will therefore study this aspect of thermal physics in detail. Here, we will briefly introduce the three modes of *heat transfer*:

- *Conduction*. There is one class of phenomena in which heat flows through bodies. The bodies do not have to move for heat to get from one place to another. Experience tells us that heat flows only from places which are hotter to those which are cooler. A difference of hotness is needed for maintaining such a flow. Indeed, bodies in thermal contact stop exchanging heat when they are equally hot. This type of transport is called *conduction of heat*.
- *Convection*. Heat can be transported with bodies. There are many examples, such as the Gulf Stream, heated water flowing from a burner to a radiator, or hot air rising up in a chimney. In this case heat does not have to flow through the bodies. Heat which resides *in* bodies flows because the bodies themselves are

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[5] Obviously, then, you will have to look elsewhere for the quantity called *heat*. This is precisely what we will do in this section. Please be patient if I use the term *heat* for the quantity which makes your room warm, which is responsible for melting ice or metal, and which drives so many of the other processes going on around us. For the impatient among you, the property emerging from our knowledge of everyday phenomena is *entropy.* I hope to motivate the properties of this fundamental thermal quantity by tying it to the concept of heat before we start using the formal term *entropy.*

transported. The driving force of the process must be the one associated with the flow of matter, for example a pressure difference. If heat is transported in this manner we speak of *convective transport of heat*.

- *Radiation*. There must be a third type of transport which, for example, manages to get heat all the way through empty space from the sun to the Earth. You can feel this kind of heat flow when you sit near a fire, or behind a window with the sun shining on you. There is no need for the air to transport heat to you. Moreover, air conducts heat much too little for this to be of any effect. Therefore, heat must flow through another medium, namely a radiation field. This type of transport is called *radiation of heat*.

Storage of heat. If heating is the rate of transfer of heat, then some *quantity of heat* is transferred in a process. If we heat a body in a particular manner, we transfer more heat the longer we allow the heating to occur. The amount of heat communicated to a body can therefore be calculated simply from the heating. In this sense, heat is a quantity which can be derived from heating; it is not new or independent of what we already have introduced.

Still, there is something new about the notion of heat, something which is not trivial at all. Heating is taken as a term for describing a process or an action. The word *heat*, on the other hand, suggests the image of something tangible, something we can measure as it flows past us when heating occurs. There is an amount of something, like an amount of water, or more like an amount of electricity which can be stored in bodies. Where else should the heat be after it has been transferred to an object in the process of heating? Why would a little child ask whether a baked potato is heavier than a cold one, if it were not for the additional heat it contains when it is hot? For this discussion we shall accept the following:

> *Heat is a quantity we can imagine as being stored in bodies, and as being capable of flowing from body to body.*

Consequently, we can say that bodies contain a certain amount of heat, and this amount can change as a consequence of heating or cooling, i.e., as a consequence of the flow of heat. For a physicist, this suggests comparisons with other quantities which have been introduced in other theories, notably those of electricity and motion (Prologue). In this sense, *heat is the extensive or fluidlike thermal quantity* (Table 4.2).

Table 4.2: Fluidlike quantities

Process	Quantity
Electric	Electric charge
Gravitational	Gravitational mass
Translational motion	Momentum
Rotational motion	Angular momentum
Thermal	Heat

Remember what I said in the first three chapters about fluidlike quantities such as electrical charge or momentum. These quantities are abstract; they are not material in any sense of the word. Still, we can profit tremendously from forming simple graphical images such as the ones used in this section. If we think of heat as an abstract "fluid," we will be led easily and directly to the formal mathematical laws that govern it. We just have to be careful not to take the naive picture too literally. Heat does not add weight to a body, it cannot be seen, nor can it be touched and, most interesting of all, heat can be produced. As we will find out shortly, this quantity is not conserved.[6]

The production of heat. We have not discussed an important question yet: Where does heat come from? Nature tells us that there must be sources of heat. In some cases heat simply flows out of bodies in the process of cooling. However, there are examples which are more interesting. Heat can come from the Sun, or out of the Earth. Heat is produced in a fire, by rubbing our hands, or by letting electricity flow through wires.

There appears to be a distinct difference between the first process, and the other ones listed above. In cooling, an object loses the heat it received in a process of heating. The body simply undergoes the reverse of the previous process. In the other cases, the body emitting the heat does not have to change its hotness. As far as we know, the degree of heat of the interior of the sun does not change much as it pours out vast amounts of heat (in fact, it gets even hotter). An electrical heater does not get cold as it heats water. And the heat produced by rubbing your hands has not been put into them previously. So, where does the heat come from in these cases?

We might believe that the amount of heat contained in bodies is always so large that the emission of some of it will not change their hotness. However, this is rather unlikely. Clearly there must be sources of heat in the true sense of the word. Heat which was not there before is pouring out of the body. Why does the electrical heater cool very noticeably when the electricity is turned off? Certainly, after switching off, it emits only a small amount of heat compared to what it emits while working. Why does the hotness change in the former case and not in the latter?

About two hundred years ago two sets of experiments were performed which were believed to demonstrate beyond any doubt that heat cannot be a conserved quantity. The first, the cannon-boring experiments of Count Rumford, have much in common with the electrical heating described above. Heat is produced by friction as long as the boring process is going on; so where does all this heat come from? The second experiment, by H. Davy, was thought to be even more important.[7] We can melt two blocks of ice by rubbing them against each other. Water which results from rubbing the ice certainly contains more heat than the ice it came from, because we need heat to melt ice. If we perform the experiment in an environment whose temperature is lower than

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[6] We are in good company with these assumptions about heat. The Greeks used a similar picture, and in early modern times up to 1850, physicists used pretty much the same ideas. Back then, heat often was called caloric (remember Carnot's description of the operation of heat engines; Section I.3). There are several other terms which aptly describe what we mean by heat: thermal element (because of the similarity to Greek thinking), or thermal charge (in analogy to electricity; see McGraw-Hill Encyclopedia of Science and Technology). Heat, caloric, thermal element, and thermal charge, refer to the same thing, namely, the fluidlike thermal quantity which flows into bodies and is stored there if the bodies are heated, and which flows out of the bodies if they are cooled.

[7] A critical reappraisal of the experiments shows that a proof of Davy's claim (Davy, 1839) was almost impossible (D. Roller, 1950). The question of where the heat comes from for melting the ice is less than trivial. However, if we could take care of all possible interferences, we would have no doubt as to whether or not we can melt ice by friction; it is certainly possible.

that of the melting ice, the heat added to the water cannot have come from outside. We have to conclude that after the process there is more heat in the world than before: the surroundings of the ice and water have not lost any heat, while the system contains more heat than before. Even though Rumford's reasoning is not tight, and Davy's experiment is difficult to perform in any quantitative manner,[8] we shall accept the evidence offered by nature: *heat can be created*.

Irreversibility. Heat can be created. Does this mean it can be destroyed as well? Since we have had to conclude that it is not a conserved quantity, the question is realistic. If we consider the evidence offered by nature, we come to the conclusion that *heat cannot be destroyed*; it can only be distributed to colder places. Heat which leaves a body goes into the surroundings to heat them. The reason why we often do not notice this effect on the surrounding bodies is simple: they usually are very much larger than the body which is losing heat.

Again, you can use your general knowledge of natural or man-made processes to come to far-reaching conclusions. You know that certain processes run one way but not necessarily in the reverse. Or if you make them run in the reverse, something else will change because of it. Real processes are said to be *irreversible*. If heat did not exist already, you would have to invent a physical quantity with its properties to account for irreversibility.

A simple example explains the meaning of irreversibility. A moving wooden block comes to rest on a horizontal surface. The reason is clear: friction hinders the motion and finally lets it "die." Friction also creates heat, so the production of heat is coupled to the block coming to rest.

What is irreversible out this? At first sight, *irreversible* should mean *cannot be reversed*. But the motion of the block can be reversed! We simply have to push the body across the surface, thereby accelerating it. Something, however, cannot be changed here: heat will also be created during the reversed motion; friction makes sure heat will be generated. You have never seen a block absorbing heat from the surroundings and destroying it, thereby starting to move by itself. This is what we mean when we say that a process is irreversible.

Another good example of irreversibility is the case discussed in Fig. 4.12. The operation of an electric water pump can be effectively reversed except for one crucial feature: the production of heat. The system that results from reversing the pump gets warm as well. Engines have to be cooled, not heated, pointing to the equivalence of irreversibility and the production of heat. Again, we can understand the behavior of some aspect of nature on the basis of the properties of heat. We now make the following definition:

> *An irreversible process is one during which heat has been created. A process without the creation of heat is called reversible.*

The term *irreversible* is somewhat unfortunate in the light of the examples given, considering that processes can be reversed with the exception of the production of heat. Another descriptive term has been coined for processes which produce heat: they are called *dissipative*.

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[8] D. Roller (1950).

The balance of heat. All in all, we form a mental picture of heat as something like a "substance" or a "stuff." We picture bodies as *reservoirs for heat*, we may speak of the *heat content* of an object, which will be described by a function of the independent variables of the body. Also, this "substance" flows into and out of bodies. The process of the *flow of heat* into a body is called *heating*. (The opposite is called *cooling*, or *negative heating*.) By stating such ideas we add heat to the list made up of electric charge, gravitational mass (gravitational charge), momentum, and angular momentum (see Table 4.2). Heat is another *fluidlike* quantity which simply means that *heat can be pictured to be contained in bodies and to flow from one body to another*. No further assumptions are made. Specifically, heat is not conserved!

All of this tells us that we should deal with heat as we do with other fluidlike quantities and formulate a law of balance to deal with its dynamics. We know how to do this from fluids, electricity, and motion (Chapters 1-3), and this will be the first step in creating a formal theory in this chapter. In contrast to the laws of balance of charge or momentum, this law will include a production term. What this means, and how this is done, will become clear in Section 4.3 and beyond.

Quantifying heat, heating, and producing heat. It is instructive to list amounts of heat to get better acquainted with this quantity (Table 4.3). As always, a physical quantity has a *unit*. Since heat is a new and fundamental quantity which is not associated with anything else we know so far, it should have its own unit. Let us therefore introduce the unit of heat called the *Carnot* (Ct) which we are going to use for now.[9]

Table 4.3: Amounts of heat (rough values in Ct)

Process or state	***S* / Ct**
Heat necessary to melt 1 cm^3 of ice	1
Heat added when heating 1 cm^3 of water from room temperature to boiling	1
Heat needed to vaporize one cm^3 of water	6
Heat content of 1 liter of gas at normal pressure and temperature	10
Heat content of 1 mole of argon gas at room temperature	10^2
Heat produced by a water heater in one minute	10^2
Heat generated when a fast travelling car brakes	10^3
Heat content of 1 liter of liquid or solid at room temperature	10^4
Heat generated in burning 1 kg of coal at room temperature	10^5
Heat escaping a standard home in one our in winter	10^5
Heat produced by 1 m^2 of a solar water heater on a sunny day	10^5

4.1.5 The Power of Heat

"Every one knows that heat can produce motion. That it possesses vast motive-power no one can doubt, in these days when the steam-engine is everywhere so well known.

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[9] For historical reasons, the unit of heat is normally given in terms of other units. In Section 4.4 we will find that it should be expressed as 1 Ct = 1 Joule/Kelvin, where Joule and Kelvin are the SI units of *energy* and *temperature*, respectively.

To heat also are due the vast movements which take place on the earth. It causes the agitations of the atmosphere, the ascension of clouds, the fall of rain….”[10]

We have seen for ourselves that heat can produce or drive other phenomena. As before, we take this as an indication of the need for a new concept, namely *energy*, that stands in a particular relationship with the quantities we use to understand a phenomenon. It is fitting that we finally deal with the field where the form of the relationship stems from: Sadi Carnot’s thermodynamics. His image of the fall of water as an analogy to the operation of heat in a heat engine (Section I.3) has served us well so far in fluids, electricity, gravity, and motion. Why shouldn’t it serve us even better in its field of origin?

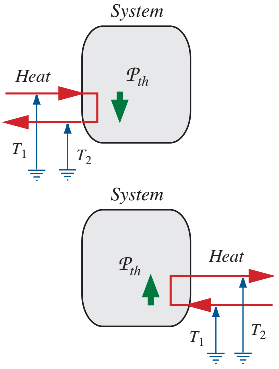

Figure 4.15: Process diagrams that explain the basic relationship of heat and energy. Top: Energy is released when heat “falls” from high to low temperature. Bottom: Energy is used when heat is pumped. The rate at which energy is released or used is called thermal power, $\mathcal{P}_{th}$.

The process diagrams that accompany the interpretations of phenomena discussed in Section 4.1.1 (Fig. 4.8 through Fig. 4.11) tell the story. There is not much to be added.[11] When heat flows from a point of high to a point of low temperature, energy is released at a rate we assume to depend upon the flow of heat and the temperature difference (Fig. 4.15, top).[12] We shall call this rate *thermal power*; it is Sadi Carnot’s *Puissance du Feu*, the *Power of Heat*. If heat is to be pumped from a lower to a higher temperature, we need energy at a rate that depends upon the rate at which heat is pumped and the temperature difference through which it is pumped (Fig. 4.15, bottom). See Section 4.4 for a quantitative discussion.

4.1.6 Heat, Thermal Processes, and the Properties of Bodies

So far, we have talked only about the generic properties of heat: it can be stored, it can flow, and it may be produced. These are the things that happen in thermal processes as far as heat is concerned. However, the interesting details of processes depend not upon heat so much as upon material bodies or systems being heated or cooled. Therefore, we will have to study in detail the special behavior of different types of physical bodies.

Different bodies contain different amounts of heat under given conditions, and different substances require different amounts of heat for melting. The form of heat flow and heat production, even the question of whether heat is produced in a particular process, will be found to depend upon the properties of the bodies suffering change. If you prefer, the answer to such questions depends upon the *models we construct of the bodies* undergoing processes.

4.1.7 Heat, Caloric, Entropy

The quantity I have been calling *heat* in the interpretations of thermal processes was called caloric by Sadi Carnot and his contemporaries. This easily visualized and intuitively understood quantity best fits what after 1850 was called *entropy* in physics, chemistry, and engineering. Therefore, the concept of entropy which, in standard presentations of thermodynamics is considered to be formal, derived, and non-intuitive,

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[10] S. Carnot (1824), p. 3.

[11] Actually, there is one thing that will be new to us, namely how to deal with the production of heat: How do we relate energy to the process of producing heat? See Section 4.4.

[12] Read Carnot’s words in the Introduction (Fig. I.3).

has simple and intuitive roots. It is analogous to volume and to charge in fluids and electricity, respectively.

What I have constructed is a generalized version of the fundamental quantity called entropy. In fact, the concept of heat used here is general enough for us to build modern continuum thermodynamics upon. The procedure is very simple. Let us accept that heat (entropy) has the properties of a non-conserved fluidlike (i.e., extensive) quantity. This will lead immediately to a law of balance of heat (entropy) as the most important expression of our assumptions about thermal processes.

From now on, the formal term *entropy* will be used for the quantity of heat. However, when speaking colloquially, I will always mean a quantity of entropy when referring to heat. In expressions such as "the body has been heated" or "in this process heat has been produced," *heat* will continue to stand for its formal equivalent, namely for entropy. Otherwise I will drop the word *heat*, i.e., I will *not* use it for the only acceptable meaning in traditional thermodynamics, namely amounts of energy exchanged in heating.

If you still believe that using the concept of entropy from the start is too difficult, consider what J. W. Gibbs once wrote:[13]

> One of the principal objects of practical research … is to find the point of view from which the subject appears in its greatest simplicity. … a method involving the notion of entropy … will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension. This inconvenience is perhaps more than counter-balanced by the advantages of a method which makes the second law of thermodynamics so prominent, and gives it so clear and elementary an expression … . If, then, it is more important for purposes of instruction and the like to familiarize the learner with the second law, than to defer its statement as long as possible, the use of the entropy-temperature diagram may serve a useful purpose in the popularizing of this science.

QUESTIONS

12. When air is compressed quickly, its temperature rises. Why shouldn't we say that the air has been heated? What could we say has happened to the air instead?
13. If a body receives 10 Ct entropy and does not lose any, does it mean that its entropy content changed by 10 Ct?
14. What is the meaning of the thermal power of a heat pump?
15. For a certain temperature difference and current of entropy, a thermoelectric device has an electric power of 1.0 W. A different thermoelectric device has an electric power of 1.2 W for the same thermal conditions. Is the thermal power different or the same in these cases?
16. A battery with an open circuit voltage of 4.5 V pumps an electric current of 1.0 A. The internal resistance of the battery is 1.0 Ω. What is the thermal power of the device? Where is the energy released/used that corresponds to this quantity?
17. When entropy flows through a copper bar, is there a measure we can call thermal power?
18. How much coal has to be burned to keep the home mentioned in Table 4.3 warm during a winter day?

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[13] J. W. Gibbs (1873).

4.2 A DYNAMICAL MODEL OF COOLING

Before we delve into a quantitative and more formal discussion of thermal processes, a dynamical model will be created for a concrete case—the cooling of hot water in a thin-walled aluminum can (Fig. 4.4, left). This should give us a better feeling for some of the questions we have to deal with in this chapter.

Hot water is poured into an aluminum can (a typical 0.5 L soda or beer can which was stripped of all its paint to reveal a polished aluminum surface). The can is placed on top of a magnetic mixer and a bar magnet is used to stir the water continuously to ensure uniform conditions. The idea is to have a single temperature of the body of water for us to deal with. The temperature is recorded as a function of time. Since the experimental result looks suspiciously like that of discharging a container or a capacitor, a model similar to those for an *RC* system (Section 1.5) might be what we need to understand the thermal phenomenon.

As before, we start constructing the dynamical model by considering appropriate laws of balance (Fig. 4.16, center). It appears that a single such expression will suffice. All we need to know is what happens to the entropy of the water. A reservoir (S_water) symbolizes the entropy of the water, and inflows and outflows represent thermal processes.

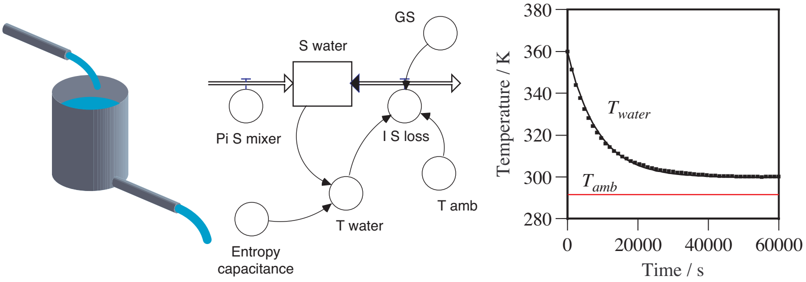

Figure 4.16: Diagram of a system dynamics model (center) and data and simulation result (right) for the cooling of hot water in an aluminum can. The hydraulic system (left) has a largely analogous structure compared to the thermal one.

There are two processes to consider: The flow of entropy out of the system (I_S_loss) which is a consequence of the difference of temperatures between water (T_water) and environment (T_amb), and the rate of production of entropy as a result of mechanical stirring (Pi_S_mixer). The former leads to the (almost perfect) exponential decay of the temperature, the latter ensures that there is a constant final temperature above that of the environment (entropy produced must leave the system). Note that we can deal with the production rate of entropy as we do with an inflow; as far as the water is concerned, produced entropy is as good as entropy transported in from outside. All in all, this looks very much like a system composed of a water tank losing water through a pipe at the bottom and receiving water through a (fixed) inflow at the top (Fig. 4.15, left). This completes the expression of the law of *balance of entropy* for the system of hot water:

$$\frac{dS_{water}}{dt} = I_S + \Pi_S \tag{4.1}$$

S is the standard symbol for entropy. This makes I_S an *entropy current* analogous to currents of other fluidlike quantities such as charge or momentum, and Π_S is an *entro-*

py production rate that measures how many units of entropy are produced every second (Π is the symbol used for production and destruction rates in this book).

At this point we need to construct ideas for the processes identified in the first step of systems analysis. From what we know of the behavior of hydraulic or electric systems, the simplest model for the loss of entropy is to make it proportional to the difference of temperatures between water and environment:

$$I_S = G_S\left(T_{amb} - T_{water}\right) \tag{4.2}$$

with a flow factor G_S (which, for obvious reasons, can be called an *entropy conductance*) as the factor of proportionality. This is the basic form of a model of a resistive transport (Section 1.4.1).

We do not yet have any experience with entropy production, so let our experience with hydraulic models be our guide to how we might get the appropriate behavior of the temperature of the system for large times (see the graph in Fig. 4.15 on the right). If we have a constant inflow that is smaller than the outflow at $t = 0$, we should expect an exponentially decreasing curve that settles above the level of the environmental temperature. So let Π_S be some constant to be determined by simulation.

This leaves the problem of how to determine the temperature of the water. We know from experience that the more entropy that is stored in the water, the higher its temperature must be. Clearly, we shall have to study this point in more detail and derive temperature–entropy relations for the materials that are of interest to us. Part of this chapter will deal with this question. The simplest possible relation is linear, meaning

$$S = KT \tag{4.3}$$

Again for obvious reasons, we should call the factor of proportionality K *entropy capacitance*. Remember the description of pressure–volume and voltage–charge relations for containers and capacitors, respectively (Section 1.4.2).

There are three parameters in this model which have to be determined if we want to compare simulations to experimental data. When we attempt simulations, a problem turns up: there is not enough information to find all three parameters independently. Say we fix the entropy production rate, we can then find the entropy conductance in this model in terms of Π_S. All we have to do is consider the steady-state toward the end of the period of the experiment when the water temperature has become virtually constant. In the steady-state, the rate of change of entropy must be zero which makes I_S the negative of Π_S. Since we know the final temperature difference $T_{amb} - T_{water}$, we can determine G_S. Once we have this, simulation of the dynamical model lets us set an appropriate value of the entropy capacitance. The results of this procedure are very encouraging (see the graph in Fig. 4.15 on the right). We get a very close agreement between data and simulations. Even though we do not have actual values of the physical parameters of the system, the ideas implemented in the constitutive laws are at least a good start.

Apparently, everything depends upon knowing how to calculate an entropy production rate which means knowing how to quantify amounts of produced entropy. Naturally, we could have started at a different point, say, by fixing the capacitance and then determine the other parameters. Either way, we need to have a clearer understanding of how bodies respond to heat. We should learn how to quantify amounts of entropy, how to determine temperature–entropy relations for simple materials, and how to find conductances for simple conductors. This is what we are going to do in more detail in the subsequent sections of this chapter.

4.3 ENTROPY AND TEMPERATURE

Hotness, or its quantitative measure called temperature, and entropy are the basic concepts we use to build thermal models. In this section, some of their formal aspects will be described, and examples of processes that can be visualized in temperature–entropy diagrams will be discussed. The examples are designed to give us an initial understanding of the use of the fundamental thermal concepts.

4.3.1 Temperature and Thermometry

Temperatures can be measured quite easily. Still, the concept of temperature is anything but trivial. In particular, we will not be able to find *the* temperature scale, i.e., the one and only scale which reads the "true" temperature. If there is anything like an *absolute temperature* independent of materials we cannot say yet. For now, we have to be satisfied with a couple of empirical scales. Some values of temperature can give us a feeling for the range of values (Table 4.4).

Table 4.4: Some temperatures (in °C)

Boiling point of helium	– 269
Boiling point of nitrogen	– 196
Melting point of carbon dioxide	– 79
Melting point of mercury	– 39
Melting point of ice	0
Temperature of human body	37
Boiling point of water (1 bar)	100
Melting point of iron	1535
Surface temperature of sun	5800
Central temperature of sun	$13 \cdot 10^6$

The Celsius temperature scale. We are quite accustomed to measuring temperatures in everyday situations. For example, if you take your temperature you might use a thermometer based on the expansion of mercury in a thin capillary. Mercury expands when it is heated, and the expansion is measured and used to fix the temperature. When bodies are heated, the rise in temperature is accompanied by changes in one or more properties. Change in volume is just one of those possible changes. Others include changes in length, electrical resistance, color, and pressure of gases.

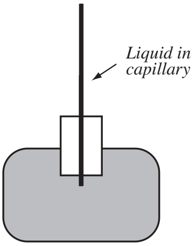

Figure 4.17: Thermometer based on the expansion of a liquid. The small changes of the volume of the liquid are made visible by the capillary.

The change of volume of a liquid can be observed using a simple device (Fig. 4.17). Fill a small bottle with the liquid and close it with a cork through which a long and thin capillary has been fitted. Allow the liquid to fill the bottom of the capillary. If you hold the bottle in your hands for a while, the liquid in the capillary will climb (in most cases). How does this work? Heat flows from your warm hands to the colder liquid, which expands. The change in volume is usually very slight, but it can be made visible by the capillary: since the capillary is very thin, even small changes in volume translate into large changes in the height of the column of liquid.

Historically, the first useful thermometers were based on this type of device. Today, we use mercury as the liquid (which we call a *thermometric substance*). On the basis of such thermometers, we may introduce a temperature scale, the *Celsius scale*. We measure the length of the column for two different temperatures, e.g., those encountered when water freezes and boils. The first point is assigned the temperature 0°C (zero degrees Celsius); the second corresponds to 100°C. The interval in the length of the column of mercury is divided into 100 equal parts, each part corresponding to a change in temperature of 1°C. The Celsius scale is not the one and only absolute coordinate system on the hotness manifold. Rather, we have arbitrarily set a certain change of temperature to be proportional to the change of length of the mercury column in the capillary.

We cannot be sure that other thermometric substances will deliver scales proportional to the one introduced on the basis of the expansion of mercury. We cannot even be sure that volume or length will always increase when the hotness increases! Water is a beautiful counterexample. Water exists in the range of temperatures spanning 0°C to 100°C. At low temperatures, near its freezing point, the volume of water first decreases, reaching a minimum at 4°C before finally increasing (Fig. 4.18). At temperatures above 4°C, water behaves as we might expect of a “normal” substance. The behavior of water at low temperatures is called an *anomaly*. This anomalous behavior prevents lakes from freezing totally, which saves the fish in them in winter.

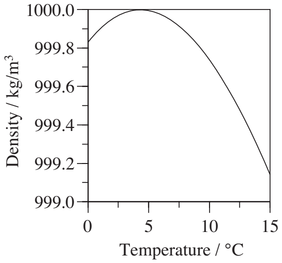

Figure 4.18: Variation with temperature of the density of water. The variation around 4°C is shown in some detail. The pressure is constant and equal to atmospheric pressure.

Water, therefore, could not be used as a thermometric substance. While we would get meaningful results out of a water thermometer in the range of temperatures from 4°C up to 100°C, the same would not be true if we included the density extremum. (The question of why we should not use water as a thermometer in the range between 0°C and 4°C is more subtle.)

Thermal expansion. Bodies expand or shrink when their temperature is increased. Fig. 4.18 shows the result of measurements of the thermal expansion (or shrinking) of water. In Fig. 4.19 the change of the length of a bar is indicated. To describe the change mathematically, it is customary to introduce a *temperature coefficient of (linear) expansion* α_l. This coefficient is defined as the relative rate of change of length l of a body with (Celsius) temperature θ. This means that the relative change of length is obtained if we integrate the coefficient over temperature:

$$\frac{\Delta l}{l} = \int_{\theta_o}^{\theta} \alpha_l(\theta)d\theta \tag{4.4}$$

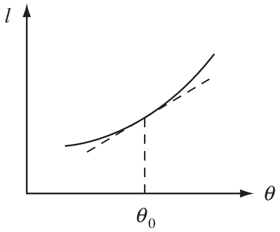

Figure 4.19: Change with temperature of the length of a long bar of a particular material. The relationship between length and temperature usually is a complicated one. Over a small range of temperatures, however, it may be approximated by a linear function.

We can approximate the length of such a bar over a small range of temperatures by a linear relation. In other words, we may choose the constant value α_{l0} at θ_0 for α_l. In this special case, the relative change of length of a body is given by

$$\frac{l - l_0}{l_0} = \alpha_{l0}(\theta - \theta_0) \tag{4.5}$$

Here, l_0 is the length of the body at a reference temperature θ_0 (which might be 0°C). Values of the coefficient of expansion for some materials are listed in Table 4.5. Note that α_l has the unit 1/K (which is introduced below).

In analogy to the formula for the change of length, the *change of volume* with temperature is often approximated by a linear expression:

$$V(\theta) = V_0\left(1 + \alpha_V\left(\theta - \theta_0\right)\right) \tag{4.6}$$

Here, α_V is the *temperature coefficient of volume expansion*; values for some materials are listed in Table 4.5. This coefficient has the unit 1/K.

Table 4.5: Linear coefficient of expansion

Substance	α_l / 10^{-6} K^{-1}	Substance	α_V / 10^{-6} K^{-1}
Copper	16.8	Alcohol	1100
Glass (pyrex)	3.2	Gasoline	1060
Glass (quartz)	0.45	Glycerine	500
Granite	3…8	Mercury	181
Ice (0°C)	0.502	Sulfuric acid	570
Iron	12.1	Water	207
Lead	29		
Sandstone	7…12		
Sodium	71		
Steel	10–16		
Teflon	60–100		
Titanium	9		

Electric resistance. Another property which in many cases changes with the hotness is the *electric resistivity* of a material. Thus it can be used for thermometry as well. A widely used thermometer is based upon the electrical properties of platinum. This thermometer is applied for accurate measurements in the range from 253°C below freezing to roughly 1200°C. Very often, the empirical relationship between temperature and resistance is represented by a quadratic equation of the form

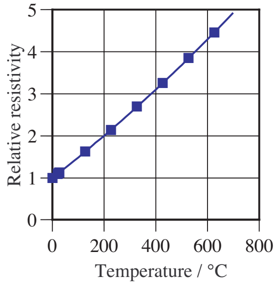

Figure 4.20: Relative electric resistivity of tungsten as a function of Celsius temperature. The reference point is 0°C.

$$R(\theta) = R_0\left(1 + \alpha_R\left(\theta - \theta_0\right) + \beta_R\left(\theta - \theta_0\right)^2\right) \tag{4.7}$$

α_R and β_R are the linear and quadratic temperature coefficients of resistivity, respectively. There is nothing deep or fundamental about the form of this relationship; it is a representation of empirical data just like Equations (4.5) or (4.6). The example of tungsten is given in Fig. 4.20. However, these equations are important in a different sense: they are examples of constitutive relations. See Table 4.6 for some data.

The ideal gas temperature. The Celsius scale of temperature is only one of many we could construct. We will now introduce another scale that will be of great use in thermodynamics, namely the *Kelvin scale*, which is based on the *ideal gas temperature* and which is independent of the particular thermometric fluid. However, we will be able to demonstrate this feature only after we have discussed thermodynamics of gases in Chapters 5 and 10.

It is a common experience that the pressure of gases increases if they are heated while the volume is kept constant. For example, consider the build-up of steam pressure in a pressure cooker: the volume does not change, and the pressure increases with increasing temperature. Somehow, the pressure of a gas must be related to its temperature. A simple setup called an *air thermometer* (Fig. 4.21) can be used to measure the temperature and pressure of a gas whose volume is kept constant. Fig. 4.22 shows the nature of the results one commonly obtains from measurements made with this apparatus (see also Fig. 4.2, right). If we draw the values of pressure as a function of (Celsius) temperature, we will find that the actual data closely follows a straight line. This behavior is interesting. (It is called the *Law of Gay-Lussac.*) Assume that air will behave in this manner at all temperatures. As a consequence, we can write the relationship between pressure and (Celsius) temperature θ in the following form:

$$P(\theta) = P_0(1 + \beta\theta) \tag{4.8}$$

where P_0 is the pressure of the gas at 0°C, and β is called the *temperature coefficient of pressure*. If we know this relationship, we can use the pressure as a measure of temperature in the interval covered by the experiment.

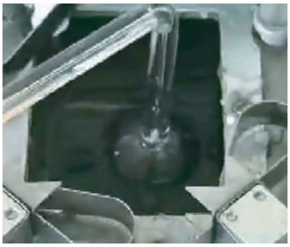

Figure 4.21: Glass bulb containing air serving as an air thermometer. The bulb is in a glycol bath whose temperature can be adjusted. The pressure of the air is measured via the capillary tube visible in the top left corner.

Table 4.6: Resistivity and temperature coefficients of resistivity (at 20°C)

Substances	Resistivity ρ / 10^{-8} $\Omega \cdot$m	Temperature coefficient α_R / 10^{-3} K^{-1}	Temperature coefficient β_R / 10^{-6} K^{-2}
Aluminum	2.8	3.9	0.6
Carbon	3500	– 0.5	
Copper	1.7	3.9	0.6
Iron	9.8	56	6.0
Platinum	10.5	3.0	0.6
Silver	1.6	3.8	0.7
Tungsten	5.6	4.1	0.96

Now there must be a temperature for which the pressure of the gas becomes zero. We find this point by extrapolating the straight line in Fig. 4.22 to lower temperatures. The pressure of a gas cannot vanish, and certainly, it cannot take on negative values. We have to conclude that this particular point must constitute a lower limit for the temperature of air.

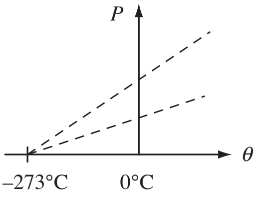

Figure 4.22: For simple dilute gases, the pressure is a linear function of temperature at constant volume. If we plot measurements for two different dilute gases, we obtain two straight lines for which $P = 0$ at the same temperature. This type of behavior is found in all gases which are sufficiently dilute and hot. The straight lines interpolating and extrapolating actual measurements represent the model of the ideal gas.

This is quite surprising in itself. It is more interesting still when we observe that all *dilute* gases show this behavior (in fact this even includes substances dissolved in others, such as sugar in water), and moreover, all extrapolated curves intersect the line of zero pressure at the same point. Measurements put the value of the temperature coefficient of pressure at 1/273.15°C for *all dilute substances*. This means that for gases showing this type of behavior irrespective of their chemical composition, there is a hotness below which the ideal gas cannot exist and this temperature is the same for all such substances! From the value of β we find that this value must be 273.15°C below the freezing point of water.

Our experience with gases which behave in this simple manner (i.e., those whose P-θ curve is a straight line) is a strong indication that the temperature found by extrapolating measurements constitutes a point of “absolute zero” for these kinds of fluids. This does not mean, however, that this temperature has any special meaning for other materials. Only further evidence can show if there are bodies which are capable of attaining hotnesses below the lowest one for dilute substances. Since we have never found such a case we believe that the value of – 273.15°C constitutes the *lowest possible value for hotnesses*.

Therefore, a natural scale of temperature would be one for which the temperature is taken to be zero at this lowest point, i.e., at – 273.15°C, and which is measured by the gas thermometer. This is done in the Kelvin scale which is defined on the following basis: zero Kelvin (0 K) corresponds to the point of absolute zero, and the interval of 1 Kelvin (1 K) corresponds to a change in temperature of 1°C. Therefore, we can convert Celsius temperatures θ into *Kelvin temperatures* T by:

$$T = \theta\,\mathrm{K}/{}^\circ\mathrm{C} + 273.15\,\mathrm{K} \tag{4.9}$$

If we use the Kelvin scale, the relationship between the pressure and temperature of gases just demonstrated takes on a particularly simple form:

$$P = P_0 \beta T \tag{4.10}$$

We call the temperature measured by the gas thermometer the *ideal gas temperature* because it is based upon the ideal behavior of dilute gases (Chapter 5). The Law of Gay-Lussac is one property of such gases. As we shall see in Chapter 5, the temperature introduced here has an important additional feature: it can be taken as the basis of a scale which is independent of the thermometric substance. It is an *absolute scale*.

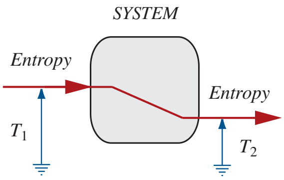

Figure 4.23: Symbolic representation of a temperature difference as the thermal driving force (of a flow of entropy).

Thermal driving force. The last point takes us back to the fundamental property of temperature. Temperature is the measure of hotness, i.e., it tells us how warm a body is; it is the *intensive* thermal quantity. Temperature differences serve as the “driving force” of the flow of entropy (by itself, entropy flows from hotter to colder places; Fig. 4.23). Expressed still differently, *temperature is the thermal potential*, and the measure of hotness introduced in the relations of ideal gases such as Equ.(4.10) serves as the proper measure of this potential. The relation between entropy and energy will be based upon it (Section 4.4).

4.3.2 Entropy

Entropy—what in lay terms would be called heat, or Carnot’s caloric—is the fundamental thermal property that is *stored* in bodies (to make them warm, melt them, expand them…), *flows* from system to system, and *is produced* in irreversible processes. I am going to list some features of entropy and discuss the only relation that deals with entropy proper and nothing else, i.e., the *law of balance* of this quantity. Applications in the rest of this chapter and this book will show the power of this concept.

Some general properties. Thermal phenomena can be understood in terms of entropy and temperature. Entropy is the technical term for what we would call heat in everyday life. It is the *fluidlike* thermal quantity that obeys a law of balance. The most important properties of entropy are:

- it can be stored in bodies,
- it can flow into and out of bodies,

- it can be produced in irreversible processes (friction, burning, electric conduction, heat flow, diffusion, absorption of light…),
- it makes bodies warm, or is responsible for melting and evaporation, or it lets air expand…
- it can work (it can release energy and drive other processes),
- or it can be pumped if energy is available (heat pump).

The first three entries in this list will appear in the law of balance of entropy. All the others relate entropy either to concrete materials and processes, or to energy.

Balance of entropy. If entropy could be stored in systems and be transported, there would be a law of balance of the forms we have seen in Chapters 1–3: The rate of change of the stored quantity is equal to the sum of all terms that quantify transfer processes. In the case of entropy, this means

$$\frac{dS}{dt} = I_{S,net} \tag{4.11}$$

(Fig. 4.24). $I_{S,\,net}$ is the sum of all entropy currents with respect to a chosen system. From our study of fluid, electric, and mechanical processes, we know the meaning of *dS/dt* and of a current of *S*. If the rate of change of the entropy is known, the *change of entropy* of the system is calculated by its integral:

$$\Delta S_{(t_1 \to t_2)} = \int_{t_1}^{t_2} \dot{S}(t)\,dt \tag{4.12}$$

As before, integrals of currents over time denote quantities *transported* or *exchanged*. In this case, the *entropy exchanged* S_e:

$$S_{e,(t_1 \to t_2)} = \int_{t_1}^{t_2} I_S(t)\,dt \tag{4.13}$$

This definition holds separately for every current as well as for the net flux (the net current yields the net amount of entropy transferred during a period of time). If we introduce Equations (4.12) and (4.13) into the instantaneous (dynamical) form of the law of balance, we obtain the expression of balance of entropy valid for a period of time:

$$\Delta S_{(t_1 \to t_2)} = S_{e,net(t_1 \to t_2)} \tag{4.14}$$

Naturally, in Equ.(4.11), we have to include all types of transfer processes having to do with conduction, convection, and radiation. We will see later (Chapter 7) how to distinguish between these different modes in the law of balance. For now, we simply assume that expressing transports in terms of entropy currents I_S is all we need.

Entropy production and the law of balance. Entropy can be produced, and this must be apparent in the law of balance. Having a non-conserved quantity is new to us— charge, momentum and angular momentum are conserved and we assumed the same to be true for volume in the fluid processes we considered. In other words, there are no production terms in the laws of balance of those fluidlike quantities. So we have to learn how to handle production of a quantity such as entropy.

Production adds to a system just as inflow does. From the viewpoint of the balance for the system there is no difference, so a production rate is a process quantity just like a current or flux, and it is added to a law of balance like a flux. There are two important differences between production rates and currents, though. The first has to do with where the quantity accumulating in the system is coming from. In the case of a current, the quantity stems from a different system which means that it will be missing there where it comes from. When a quantity is produced, though, it will not be missing anywhere else; it literally comes from nowhere and simply appears on the scene. The second distinction between currents and production rates is mathematical. Production happens inside a system, and it is distributed over the inside, normally over a volume. A current, on the other hand, quantifies a transport across the systems' surface (a 2D-boundary). When we treat spatially non-uniform (continuous) systems in Parts III and IV, this distinction will become crucial. It means that a production rate has a (volume) density, whereas a surface density is associated with a current.

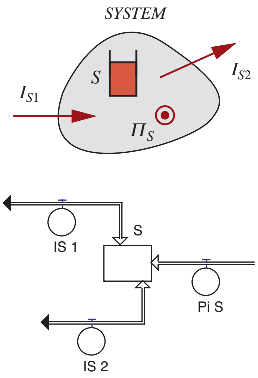

Figure 4.24: Balance of entropy. Top: Process diagram showing storage, flows, and production of entropy. Bottom: System dynamics diagram of the corresponding law of balance.

The process of entropy production can be quantified by a production rate Π_S and by the entropy produced in a process during a specified period of time for which I use the symbol S_{prod}. The two are related by

$$S_{prod(t_1 \to t_2)} = \int_{t_1}^{t_2} \Pi_S(t)\,dt \quad , \quad \Pi_S \geq 0 \tag{4.15}$$

The law of balance of entropy can now be expressed in dynamical form (Fig. 4.24):

$$\frac{dS}{dt} = I_{S,net} + \Pi_{S,net} \tag{4.16}$$

and in integrated form as it applies to a period of time:

$$\Delta S_{(t_1 \to t_2)} = S_{e,net(t_1 \to t_2)} + S_{prod,net(t_1 \to t_2)} \tag{4.17}$$

These are general forms of the law of balance of entropy (for the moment we disregard the question of how different transfer processes should be dealt with, Chapters 7-8).

Entropy producing processes. Where, when, and how is entropy produced? Everyday experience is a relatively good guide when it comes to identifying entropy sources. The major culprits are clear: mechanical friction, letting electricity flow through wires, and burning fuels. Several of the remaining important entropy producing phenomena can be identified by analogy with the flow of electricity and with friction. We know that heat is produced in resistive processes which we have been able to explain in terms of conductive transports of momentum and electricity (Chapters 1 and 3). If we take these processes as a guide, two more phenomena turn up as producing heat: the conductive transports of heat and of substances, i.e., diffusion of heat and substances. The former will play an important role in this and some of the following chapters in our treatment of heat transfer; the latter is central in physical and living systems and will be dealt with in Chapter 6. This leaves one highly irreversible processes to be listed: the absorption and emission of radiation which is fundamental to an understanding of the interaction of our planet with solar radiation (Chapters 7 and 15).

Since entropy production requires a driving process that makes energy available, the relation between energy and entropy lets us be precise about how to identify and quantify irreversibility. This issue will be taken up below in Section 4.4.

4.3.3 Thermal Processes and *TS* Diagrams

In this section I will describe a few simple thermal processes. By looking at some interesting cases we will learn to better understand the nature of heat (entropy). As examples, I shall choose two classes of thermal processes that have played a major role in the early development of thermodynamics.

Our first example is *heating or cooling of simple fluids, such as air, whose volume and temperature can be changed.* If we put air in a cylinder having a piston we have a device which lets us compress or expand the gas. At the same time, the air might be heated or cooled. (See Fig. 4.25.) We are interested in the exchange of entropy, and the change of the entropy content; i.e., we will try to *account for amounts of entropy*. Naturally we also want to know what happens to the *hotness* of the fluid. To make things as simple as possible, we shall conceive of *reversible* operations, i.e., processes which conserve entropy.

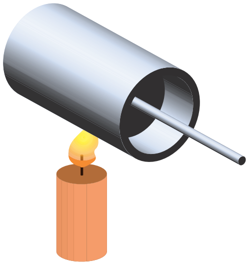

Figure 4.25: A simple device which allows us to put a fluid such as air through thermomechanical processes, i.e., processes which couple thermal and mechanical operations only. The volume may be changed with the help of the piston, and heating and cooling may be present.

The second example is *the melting or vaporization of single substances.* Again we want to understand what happens to the entropy and temperature of the materials.

Adiabatic compression and expansion. Let me begin with a phenomenon which might appear rather surprising at first. Consider the special case of air in a cylinder having a piston. The setup is assumed to be perfectly insulated which makes the exchange of entropy impossible. We are allowed only to compress or expand the air. If this condition is satisfied, we say that the fluid may undergo only *adiabatic processes*. We know from experience with bicycle pumps that upon sudden compression, the temperature of the air rises abruptly (Section 4.1.1, Fig. 4.3). On the other hand, if the gas is allowed to expand under such circumstances it is found that the temperature drops steeply. In other words, in adiabatic compression or expansion of a fluid such as air, its hotness changes without heating or cooling.

To many observers this is surprising indeed. Would we not automatically believe that some heating must have occurred for the temperature of a body to increase? Heat has not been exchanged because of the perfect insulation, which in the case of a bicycle pump, may be simulated by performing the compression so suddenly that heat does not have any time to flow. We also assume that there are no sources of entropy as a result of friction. The theory of adiabatic reversible processes presented in Chapter 5 shows that the changes of hotness are a natural result of the change of volume of a fluid. Experiments beautifully verify this point.

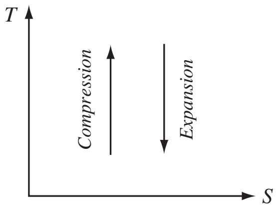

Figure 4.26: Adiabatic compression and expansion in the temperature-entropy diagram. This diagram is a valuable tool in thermodynamics as was observed by J.W. Gibbs (see Section 4.1.7).

In summary, the temperature of air changes upon compression or expansion without any heating having taken place and without any internal sources having supplied entropy. In other words, the entropy content of the gas must remain constant during adiabatic reversible changes. This is a simple case of accounting for amounts of entropy: nothing has gone in, nothing has come out, and nothing has been produced inside. There is a simple and useful tool which allows us to describe this phenomenon graphically, namely the *temperature-entropy diagram* (or *TS* diagram) of the process (Fig. 4.26). Since the entropy content of the body remains the same, the curve representing the process must be a vertical line in the diagram. The temperature rises upon compression, and it decreases as a result of expansion of air.

If for any reason the process considered is not reversible, i.e., if heat is generated in the fluid, the representation of an adiabatic change in the *TS* diagram will differ from the one in Fig. 4.26.

Heating at constant volume. Next, consider the heating of air if its volume is kept constant. We say that under these circumstances the fluid undergoes an *isochoric process*. It is very simple to keep the volume constant in the case of gases heated or cooled. Heat does what we usually believe it does. A body which is heated at constant volume gets hotter. Experience tells us that no matter what kind of body is heated at constant volume its temperature must increase if heat is absorbed, and it must decrease if heat is emitted.

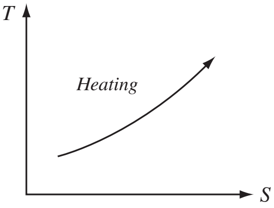

Figure 4.27: Heating at constant volume. If entropy is added, the temperature of the body must increase. How it increases depends on the properties of the body.

Again, we can try to exhibit the process in the temperature-entropy diagram. Only here we have a real problem which cannot be solved without knowledge of the constitutive properties of the body: What is the concrete relationship between temperature and entropy content as entropy is added or removed? Since we do not have this information at this point, all we can do is give a qualitative impression of what the relationship might look like (Fig. 4.27). Below we will introduce a constitutive quantity which describes bodies heated in such a manner. This quantity is called the *entropy capacitance*. It measures how the temperature changes with the change of the entropy of the body.

Since we assume entropy to be conserved we know that the amount of entropy communicated to the body is equal to the change of its entropy content. Again, this is a particular case of accounting for entropy: the entropy content of a body can change by transfer only, since nothing is produced inside. The sum of what has been absorbed and emitted must be equal to the change of the contents.

Isothermal processes. Another interesting process is the heating of air at constant temperature. We speak of *isothermal processes* in this case. Since the temperature of air changes if it is heated at constant volume, we obviously have to let the volume change for an isothermal process to take place. On the other hand, we have seen that the temperature changes if the volume is changed without heating (adiabatic processes). Combining these experiences we can come up with the answer of how to perform an isothermal process. We may heat a body which would normally increase its temperature; if we let the fluid expand, its temperature should drop. We only have to combine and fine-tune the rates of heating and of expansion for the temperature to remain constant (Fig. 4.28). On the other hand, the hotness of air rises if it is compressed without heating. Therefore, we must cool it at just the right rate during compression for the temperature not to change. In summary, if a fluid such as air is to undergo an isothermal expansion it has to be heated at the same time; during an isothermal compression it has to be cooled. Therefore, if the volume of air increases isothermally its entropy content increases; entropy is literally sucked up by the gas. If the volume decreases the entropy content decreases; entropy is pressed out of the fluid like water out of a sponge.

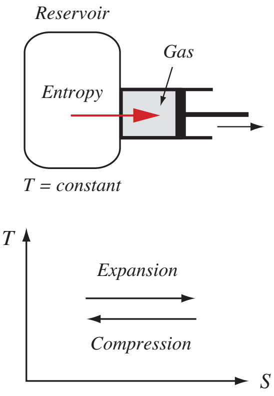

Figure 4.28: If a gas is to expand or contract at constant temperature, it has to be able to exchange entropy with the surroundings. The processes of isothermal expansion or compression are represented by horizontal lines in the *TS* diagram. On expansion, fluids usually absorb entropy. However, this does not always have to be the case: water in the range of temperatures between 0°C and 4°C behaves differently!

There is an important exception to the details of adiabatic and isothermal processes just presented. Water in the range of temperatures between 0°C and 4°C behaves differently. Take the isothermal changes first. Water will be found to *emit* heat when *expanding* at a temperature in this range. Also, for part of an adiabatic compression the temperature decreases as the volume is decreased, only to go through a minimum whereupon it increases as is normally expected.[14] Even though there are very few cas-

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[14] Kelvin was one of the first to discuss the significance of this behavior for thermodynamics (see Truesdell, 1980). A theory of classical thermodynamics allowing for the anomaly was first presented by Truesdell and Bharatha (1977).

es of anomalous behavior, the example of water demonstrates that we cannot simply leave it out of our considerations. Water is too important a fluid.

We would like to know how much entropy is required for a given change in volume of the fluid. Again this question is answered by a particular constitutive quantity, which is called *latent entropy*. It will be introduced in Chapter 5.

Melting and vaporization. Finally, let us take a brief look at *phase changes*. When a block of ice having a temperature below the freezing point is heated, we first observe a rise of temperature of the body (Fig. 4.6). The process is analogous to the heating of a fluid at constant volume (Fig. 4.27). The water which is produced from the ice by melting behaves similarly. We also know that water eventually turns into steam, which can be heated further at constant volume if we like. But what about the processes which turn ice into water, and water into steam?

If we monitor the temperature of ice, water, and steam as we add heat (see Fig. 4.6 and Fig. 4.29), we observe that the melting of ice and the vaporization of water take place at *constant temperatures*: they are *isothermal processes*. Again, this is a rather surprising result. Without thinking about it we often assume there to be a change of temperature during the heating of a mixture of ice and water, or of water and steam. However this is not true. As in the case of the isothermal heating of fluids, the entropy entering a body does not do what we think it normally does: it does not raise the temperature of the body.

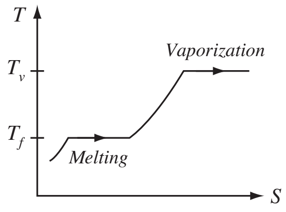

Figure 4.29: Relationship between temperature and entropy for melting or vaporization of ice and water. During the change of phase, the temperature of the body stays constant. The diagram gives only a qualitative representation of the relationships. (T_f: melting point, T_v: temperature of vaporization.)

The melting of ice has played an important role in the history of the theory of heat. The process served as a means for constructing ice calorimeters, and the melting of ice by rubbing two blocks of it against each other provided strong evidence that entropy can be created (Section 4.1.4).

As we have seen several times, the examples of adiabatic and isothermal changes clearly demonstrate that heat and hotness cannot be the same quantities. In one case, the hotness changes even though the entropy content does not; in the other, the amount of entropy in a body changes while the temperature remains constant.

QUESTIONS

19. What relations from electricity are analogous to Equ.(4.2) and Equ.(4.3)?
20. What observation suggests that an expression of the form given in Equ.(4.2) might be appropriate for a flow of entropy out of a hot body?
21. Why is water a bad thermoscopic material?
22. What observations suggest that hotness has a lowest possible value? Is an "absolute zero" point a general property of intensive quantities known from fluids, electricity, or motion?
23. Why does it make sense to assume that diffusion is an entropy producing process?
24. If there is a net *inflow* of entropy into a body, is it possible for its entropy to decrease?
25. If the sum of all currents of entropy with respect to a body is positive, is it possible for the body to get colder?
26. What is the *TS* diagram of adiabatic compression of a gas with internal friction?
27. Why is the representation of isothermal expansion of a gas a horizontal line to the right in the *TS* diagram?
28. What is the *TS* diagram of freezing of water? What does this mean for the entropy content of the system and entropy exchanged by the system with its environment?

EXAMPLE 4.1. Accounting for entropy.

Due to some irreversible process, entropy is produced in a body of water at a rate that increases linearly from 1.0 Ct/s to 1.5 Ct/s in 100 s. It is observed that the temperature of the water does not change (there are no phase changes!). (a) What is the rate of change of entropy of the body? (b) Are there any entropy currents with respect to the body of water? If so, how large are they? (c) How much entropy has been produced in these 100 s? (d) How much entropy has been exchanged with the environment? (e) What happens to the entropy of the body if it is thermally insulated?

SOLUTION: (a) Since water is a material whose temperature only changes if its entropy is changed, constant temperature means constant entropy. The rate of change of entropy is equal to zero. (Water has a very small compressibility which changes the result slightly.)

(b) If the rate of change of entropy is zero, the (net) entropy current is equal to the negative entropy production rate:

$$\dot{S} = I_{S,net} + \Pi_S \quad , \quad \dot{S} = 0 \quad \Rightarrow \quad I_{S,net}(t) = -\Pi_S(t) = -\left(1.0\frac{\text{Ct}}{\text{s}} + 0.0050\frac{\text{Ct}}{\text{s}^2}t\right)$$

(c) The entropy produced equals the integral over time of the production rate. Here, the integral of the entropy production rate over time is equal to 125 Ct.

(d) We can integrate the (net) entropy flux to obtain the entropy exchanged. Alternatively, we can apply the integrated form of the law of balance:

$$0 = S_{e,net} + S_{prod} \quad \Rightarrow \quad S_{e,net} = -S_{prod} = -125\text{Ct}$$

(e) Thermal insulation prevents the exchange of entropy of a body with its environment. If the body of water is thermally insulated, and if we have the entropy production rate as described here, the entropy of the body must change according to

$$\dot{S} = I_{S,net} + \Pi_S \quad , \quad I_{S,net} = 0 \quad \Rightarrow \quad \dot{S}(t) = \Pi_S(t) = 1.0\frac{\text{Ct}}{\text{s}} + 0.0050\frac{\text{Ct}}{\text{s}^2}t$$

In 100 s, the entropy of the body increases by 125 Ct.

EXAMPLE 4.2. Replace an adiabatic process by isochoric and isothermal steps.

Air in a bicycle pump is compressed adiabatically. How can the air be brought back to its original state if we first wait for the air to cool in the pump? Draw the steps performed in a *TS* diagram.

SOLUTION: If we compress air adiabatically, we raise its temperature without changing its entropy content (see figure). If we now wait for the air to cool without the piston being moved, the following will take place: Entropy flows out of the air at constant volume, thereby reducing its temperature. This step restores the initial temperature to that of the surroundings, but it reduces the entropy of the air. Therefore, as a last step, we have to increase the entropy content to its original value without changing the hotness of the system. This is achieved by isothermal heating which also brings the volume of the air back to its initial value.

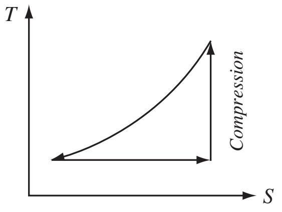

Figure Ex.2

EXAMPLE 4.3. Irreversible adiabatic processes.

A certain amount of gas is put in a cylinder having a piston and which is perfectly insulated against the flow of heat. The gas is first compressed and then allowed to expand again to the point where the temperature regains its initial value. The processes undergone by the gas are supposed to be irreversible, possibly because of viscous friction in the fluid. Is the volume at the end smaller than, equal to, or larger than that at the beginning? Write the equation of balance of entropy for adiabatic irreversible processes, and display the operations in the *TS* diagram.

SOLUTION: Because of the ideal insulation, the processes are adiabatic; i.e., there is no exchange of entropy. For this reason, the flux term in the equation of balance of entropy is equal to zero. The production term is not equal to zero, though, which leads to the following equation of balance of entropy:

$$\dot{S} = \Pi_S$$

Thus, the entropy of the body can only increase.

In a gas, the temperature increases as the result of adiabatic compression. Entropy is produced at the same time. Therefore, the amount of entropy in the system increases as the temperature rises, and the process is represented by a curve such as the one shown in the *TS* diagram. (Note that we do not have any information regarding the properties of the gas. For this reason we cannot actually calculate the details of the processes. The curves displayed in the *TS* diagram are to be taken only as a qualitative description of what is happening.)

The second step is an adiabatic expansion, which leads to a lower temperature. Again the process is irreversible, which causes entropy to be produced. When the initial temperature is reached, it stops. Compared to the beginning, there is more entropy in the gas at the same temperature. We have seen in Section 4.3.3 that for most substances (with the notable exception of water in the range between 0°C and 4°C) the volume increases if entropy is absorbed at constant temperature. The combined adiabatic irreversible steps are actually equivalent to isothermal heating. Therefore, the volume is expected to be larger at the end than at the beginning.

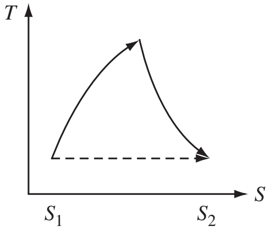

Figure Ex.3

4.4 ENERGY IN THERMAL PROCESSES

There are two main points to be discussed when energy is introduced to a new field. First, what is the relation of energy to the basic quantities used to model processes in the new field? Here, these quantities are entropy and temperature. Second, we have to answer the question of how the law of balance of energy changes if thermal processes are included. The former question is answered by appealing to analogies of thermal processes with other phenomena. The latter has an even simpler answer: Thermal processes, like any other phenomena, allow for the exchange of energy. Therefore we simply include a new type of energy exchange in the law of balance of energy by adding a term.

4.4.1 Balance of Energy Including Thermal Processes

Why can we be certain that thermal processes involve energy exchanges? The reasoning is simple. Thermal processes couple to other phenomena. Take the example of electric heating at one end of a copper bar (Fig. 4.5). If we do not want to suddenly change what we believe applies to energy in electric processes, we must conclude that energy is transferred from the electric wires together with the entropy produced in these wires. The balance of energy for the electric heater tells us this much. So if we consider the transfer of the entropy produced in the wires a thermal process, we can say that energy is transferred in thermal phenomena as well. The story can be continued by considering what happens to the entropy passed from the electric system to the heated end of the copper bar. Conduction in the bar tells us that entropy flows from a hotter to a colder element. It should not matter if an element is heated electrically or by contact with a hot part. If energy is transferred with entropy in the first case, it will be transferred in the second example as well.

In summary, energy transfer accompanies entropy transfer in thermal processes. The change of the law of balance of energy including thermal phenomena is simple and minimal: We have to add an energy transfer term for the new type of phenomenon. We have used energy currents in fluid, electric, or mechanical phenomena to quantify energy transfer. Now we add a current of energy to quantify energy transfers as a consequence of heating or cooling:

$$\frac{dE}{dt} = I_{E,fluids} + I_{E,el} + \ldots + I_{E,th} \tag{4.18}$$

$I_{E,th}$ represents the new term which refers to *energy transfers in heating and cooling*; E is the energy stored in the system whose energy balance is being considered. Remember that heating and cooling refer to entropy flows from hotter or to colder bodies—relative to the body we are dealing with.[15]

As with all laws of balance, there is an integrated form which may be applied to processes lasting for a certain period of time $t_1 \rightarrow t_2$:

$$\Delta E_{(t_1 \rightarrow t_2)} = E_{fluid(t_1 \rightarrow t_2)} + E_{el(t_1 \rightarrow t_2)} + \ldots + E_{th(t_1 \rightarrow t_2)} \tag{4.19}$$

The remarks made about $I_{E,th}$ also apply to E_{th}. So far, the term E_x has been used to denote quantities of *energy transferred* in a process (Section 2.4.1). This usage will be continued with thermal processes. Therefore, E_{th} is the symbol for amounts of *energy transferred in heating or cooling* of bodies.[16]

4.4.2 Entropy, Temperature, and Energy

We might expect to be able to learn more about entropy if we manage to clarify its relation to energy in thermal processes. In his investigation of the motive power of heat, Carnot was the first to see this important point. We shall attack the problem head on by employing the full power of his comparison of heat and water (Section I.3 and

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[15] This statement is not as innocent as it may sound. What is a thermal process actually is open to debate. Should we include the transfer of entropy stored in a heated fluid together with that heated fluid, as in a central heating system? Or should this be regarded a fluid process? In fact, it is simpler to take the latter point of view and to exclude fluid transfer and even radiation from the list of proper thermal processes. This leaves conduction of entropy, and this is how $I_{E,th}$ in Equ.(4.18) will be interpreted: it is the energy current accompanying conductive entropy transfers. Conduction of entropy is the narrowest but simplest and clearest definition of heating and cooling.

[16] After about 1850, the quantity E_{th}, which denotes amounts of energy transferred in heating or cooling, was given the name "heat." The symbol Q is commonly used for this quantity in thermal physics. Since I do not associate more meaning with an amount of energy transferred in heating or cooling than with any other quantity of energy transferred in whatever process we might study, I refrain from using specialized symbols. More importantly, however, it is less than helpful to use the conventional word *heat* for the last term in Equ.(4.19), i.e., for a quantity having to do with energy. As discussed in Section 4.1.4, energy plays an altogether different role than the one associated with it in traditional thermodynamics.

Section 4.1.5). We will assume that the role of energy in thermal processes is the same as that known from other fields of physics as discussed in Chapter 2. In summary, Carnot's investigation of the principle of operation of heat engines will deliver the following results:

1. A heat engine absorbs entropy from the furnace at higher temperature; if it could be operated reversibly, the same amount of entropy would be transferred to the cooler, i.e., to the environment at lower temperature.
2. By lowering entropy from a point of higher temperature to a point of lower temperature, energy is released at a certain rate (thermal power); this energy drives the mechanical process.
3. The energy released when entropy falls is supplied to the engine with entropy from the furnace. More generally, energy is transferred together with entropy in heating and in cooling.

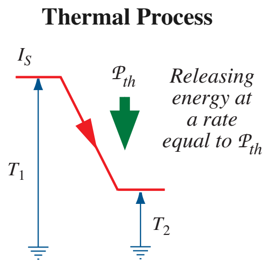

Figure 4.30: Waterfall image of a thermal process: Entropy falls from a point of high temperature T_1 to a point of lower temperature T_2, thereby releasing energy at a well defined rate.

In short, we simply add thermal phenomena to the list of processes known from other areas of physics. Accepting this, we will be able to directly state the formula for the motive power of heat, which will provide for the simplest possible entry into thermodynamics. (A derivation on the basis of some other assumptions can be found in Chapter 10.) The consequences of this idea will be developed for ideal engines and for entropy production in the present section.

Thermal power. On the basis of these observations regarding the operation of heat engines, Carnot was able to suggest a theory relating heat and energy. We already have presented the basic idea of how such engines work, by the usual *waterfall diagram* and associated process diagrams in Fig. 4.15. Therefore, in analogy to other fields of physics, we should expect the motive power of heat engines to be strictly proportional to the drop of the thermal potential. Compare the process depicted in Fig. 4.30 to the operation of a hydromechanical engine, i.e., a water turbine which is driven by water falling from an artificial lake at a high level, or any other type of engine. This immediately lets us write the thermal power in the form

$$\mathcal{P}_{th} = -\left(T_2 - T_1\right) I_S \tag{4.20}$$

Entropy can be *pumped* like water, and as in the case of water the rate at which energy is used to pump a current of entropy is also given by Equ.(4.20).

Energy transfer in heating and cooling. A few simple but important facts are known about heat engines: First, they need a furnace and a cooling device; i.e., they operate between two environments at different temperatures; they absorb heat from the furnace, and they emit heat to the cooler. Second, the motive power of such engines depends on the temperatures of the furnace and the cooler; indeed, their power increases with an increasing difference between the upper and the lower temperatures.

Let us now turn to the first of these observations. Heating the engine first of all means that entropy is taken in from the furnace at the higher temperature. Since entropy cannot disappear, it has to be emitted if the engine is to operate steadily. This is accomplished with the help of the cooling device receiving the entropy rejected by the engine. We know from the properties of entropy that the current leaving the engine must be equal to that entering if all the operations are reversible, i.e., if entropy is not produced in the system. Since cooling takes place at a lower temperature, entropy flows from the hot furnace to the cooler and we say that heat engines are driven by the *fall of heat* (entropy). Temperature therefore plays the role of the *thermal potential*.

This we have seen already, but the discussion points to an additional aspect of energy in thermal phenomena. The entropy that is taken from the furnace carries with it some energy (Fig. 4.31), and the entropy emitted to the cooler also takes some energy along. If this were not the case, where would the energy released in the fall of entropy come from?

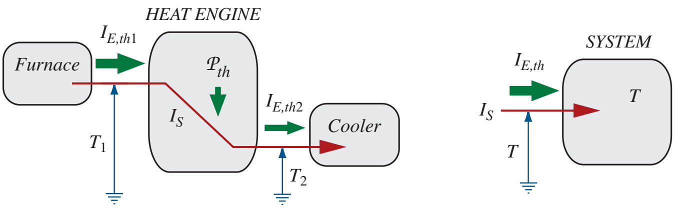

Figure 4.31: Left: Part of the process diagram of a heat engine. Energy is supplied and removed along with entropy coming from the furnace and leaving to the cooler. Note that nothing has been said about what the energy released is used for. Right: Symbolic representation of heating (or cooling) of a system at temperature T.

It makes sense to assume that the energy released is the difference of energy delivered and removed at high and low temperature, respectively. Therefore, we should calculate an energy current carried by an entropy current in heating or cooling of bodies by:

$$I_{E,th} = T I_S \tag{4.21}$$

This is in complete analogy to what we have used in fluid, electric, and mechanical processes before (see Chapters 2 and 3). So there is an additional interpretation of entropy: it is the *carrier of energy in heating and cooling*.

If we wish to know how much energy has been transferred in a process of heating or cooling, and if we want the relation of this quantity to entropy and temperature, we simply integrate Equ.(4.21) over time:

$$W_{th} = \int_{t_1}^{t_2} T I_S dt \tag{4.22}$$

Entropy production and dissipation. The qualitative discussion of entropy production and irreversibility in Section 4.1 should have made it clear that while entropy appears out of the blue, it does not do so on its own. There have to be processes that drive the production of entropy. Such processes are called irreversible or *dissipative*.

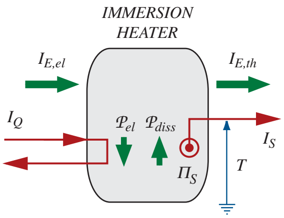

Figure 4.32: Process diagram of an immersion heater. The energy released in the electric process is completely dissipated (used to produce entropy).

Generally, voluntary processes cause more than a single phenomenon. A water pump is built to pump water, and the energy released by the driving process is expected to go mostly toward the process the device was designed for. Invariably, however, part of the energy released drives the production of entropy—engines heat up and they have to be cooled. The part of the energy made available that is used for entropy production is said to be *dissipated*.

Equations (4.20) and (4.21), i.e., the relations for thermal power and energy currents in heating and cooling, allow us to calculate the energy needed to produce entropy at a given temperature. Consider a totally dissipative device such as an electric heater whose process diagram is shown in Fig. 4.32. Energy is supplied to the heater and is released in an electric process. Since the heater drives a single process—entropy production—all the energy released is dissipated; it drives the thermal process of producing entropy. As a consequence, the rate at which energy is dissipated is known; it is the thermal power of the process. The dissipated energy is then emitted by the heater together with the entropy that was produced. In summary, we can say that

$$\mathcal{P}_{diss} = T\Pi_S \tag{4.23}$$

When entropy is produced at temperature T at a rate Π_S, we need energy at the rate given by Equ.(4.23); this is called the *dissipation rate* $\mathcal{P}_{diss}$.[17]

4.4.3 Heat Engines and Heat Pumps

Combining everything we have learned so far—balances of entropy and of energy, and the relation between entropy, temperature, and energy—will allow us to come up with some rather interesting and useful results regarding the operation of thermal engines in spite of the generality of the relations. More detailed models will require the study of particular constitutive laws of components making up real engines (see Chapters 9 and 15).

Ideal heat engines and heat pumps. When entropy flows through an engine from points of high to points of low temperature (from a burner to a cooler), energy is released (see Fig. 4.30). If all the energy that is released is used to drive the desired process (mechanical, electrical, etc.), the engine is said to be *ideal*. Ideal engines are non-dissipative. In this case, the process diagram of a heat engine takes the form shown in Fig. 4.33 (left). For heat pumps and refrigerators where entropy is pumped from lower to higher temperature, all we have to do is reverse the flows of fluidlike quantities and change the signs of potential differences (Fig. 4.33, right). If all the energy released by the driving process is used to pump entropy, the heat pump is said to be ideal.

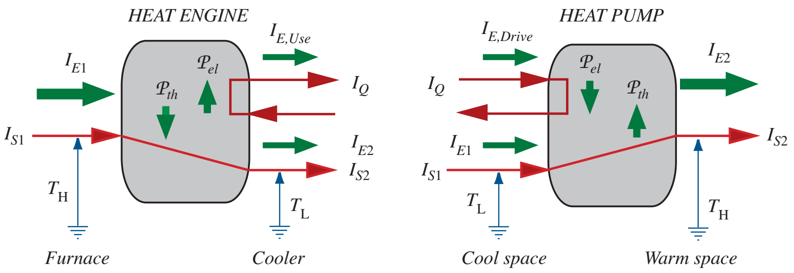

Figure 4.33: Process diagram of an ideal heat engine (left) and an ideal heat pump (right). Ideal means that there is no entropy production in the engines.

Here is a complete analysis of the ideal heat engine at the level of general relations discussed so far. There is one expression for the balance of entropy and three relating to the energy principle:

$$0 = I_{S1} + I_{S2} \tag{4.24}$$

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[17] To end up with proper signs, the dissipation rate has to be defined as the negative thermal power of the process of producing entropy. When entropy falls and releases energy (Equ.(4.20)), the power is positive, so in an involuntary thermal process where energy is used the power is negative. The dissipation rate, however, needs to be a positive quantity.

$$\begin{aligned} 0 &= I_{E1} + I_{E2} + I_{E,use} \\ 0 &= \mathcal{P}_{th} + \mathcal{P}_{el} \\ I_{E,use} &= -\mathcal{P}_{el} \end{aligned} \tag{4.25}$$

(Note that these relations hold for the steady-state.) We add to this the relations between entropy currents in heating and cooling and the associated energy currents:

$$I_{E1} = T_{\mathrm{H}} I_{S1} \quad , \quad I_{E2} = T_{\mathrm{L}} I_{S2} \tag{4.26}$$

Efficiencies. It is customary to introduce two measures of efficiency that can be derived from the foregoing. The first is the ratio of useful energy current to energy supplied by the burner (called the *thermal efficiency* or *first law efficiency*):

$$\eta_{\mathrm{I}} = \left| I_{E,use} / I_{E1} \right| = \frac{T_{\mathrm{H}} - T_{\mathrm{L}}}{T_{\mathrm{H}}} \tag{4.27}$$

The second is the ratio of useful power to thermal power (called the *second law efficiency*):[18]

$$\eta_{\mathrm{II}} = \left| \mathcal{P}_{el} / \mathcal{P}_{th} \right| \tag{4.28}$$

For an ideal heat engine (Fig. 4.33, left), the second measure of efficiency is equal to 1. It seems to be the more natural and intuitive of the two measures. It tells us how well the engine performs, measured relative to what nature allows. We can only use the energy made available by the fall of entropy, i.e., $\mathcal{P}_{th}$.[19] If we can use all of it, we have designed a perfect engine. Moreover, Equ.(4.28) represents the same type of efficiency measure as those used in other devices such as pumps, turbines, motors, etc.

The so-called first law efficiency or thermal efficiency is commonly used to report the performance of heat engines; for example, the thermal efficiency of a large nuclear power plant is little more than 30%. For *ideal engines*, the efficiency is given by Equ.(4.27) which is called the *Carnot efficiency* η_C of heat engines. It is the highest possible value of thermal efficiency that can be achieved by any thermal engine running between a furnace at T_{H} and a cooler at T_{L} (H and L stand for high and low, respectively). This point will be discussed further below and again in Chapter 5.

It is important to realize that η_{I} is smaller than 1 no matter what we do unless we could build a cooler at the lowest possible temperature of 0 K. This is true even for non-dissipative engines, and, as we shall see shortly, even for the best of them, the Carnot engine. The reason for this is simple to understand if we consider the balance of entropy rather than just the balance of energy. Since the entropy supplied to an engine has to be emitted to the cooler, it will take a current of energy equal to $T_{\mathrm{L}} I_S$ into the environ-

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[18] In Section 4.4.5, a brief description of what are termed First Law and Second Law of thermodynamics will be given. This should explain where the names first law efficiency and second law efficiency come from.

[19] In a fall of water in the Swiss Alps, we can only use the energy released which is proportional to the height difference. The level of the environment at the foot of the mountains defines the lowest possible point water can reach even though we can imagine the water to fall still further on its way in the river to Holland.

ment (Fig. 4.33, left). This is simply unavoidable.[20] It is not the fault of engineers who do not understand nature well enough.

There is actually a good reason for using the first law efficiency in Equ.(4.27) alongside the more intuitive measure in Equ.(4.28). The loss of energy to the environment actually starts when we produce the entropy that runs the heat engine by burning some fuel or splitting nuclei. The entropy produced must end up in the environment eventually. There is irreversibility here, just not in the engine but in the furnace. Carnot's formula accounts for this in the case of ideal engines, where "ideal" means that the core of the engine is non-dissipative.[21]

Coefficient of performance. Let us now briefly turn to *heat pumps*. For heat pumps, one introduces the *coefficient of performance* which is the ratio of the useful energy current—the energy current accompanying the entropy flow that heats the warm space (Fig. 4.33, right)—to the power of the driving process. If we perform a derivation analogous to what was done for engines, we get the *coefficient of performance* (*cop*)

$$cop = \left| I_{E2} / I_{E,drive} \right| = \frac{T_{\mathrm{H}}}{T_{\mathrm{H}} - T_{\mathrm{L}}} \tag{4.29}$$

which is the inverse of the Carnot efficiency in Equ.(4.27). The result has been derived for ideal engines (real heat pumps do not even come close to this value). For refrigerators, the figure of merit is the ratio of the energy current removed from the cold space to the driving power, so the equations is different from Equ.(4.29).

Just as the first law efficiency η_1 of a heat engine, Equ.(4.27), might give the wrong impression of the performance of a thermal engine, the coefficient of performance introduced in Equ.(4.29) tells only half the story. A better way of measuring the efficiency of heat pumps and refrigerators is to compare the thermal power for lifting entropy to the actual mechanical or electrical power of the engine:

$$\eta_{\mathrm{II}} = \left| \mathcal{P}_{th} / \mathcal{P}_{el} \right| \tag{4.30}$$

This is a figure analogous to the second law efficiency of heat engines. Note that it is the inverse of what was defined in Equ.(4.28), just as the coefficient of performance is the inverse of the Carnot efficiency. Naturally, for ideal heat pumps and refrigerators, the efficiency η_{II} is equal to 1; otherwise it is lower than 1.

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[20] This non-intuitive measure(η_{I}) has caused people to wonder why this should be so, or if it should be so at all. A cottage industry of inventors has developed that tries to design engines that use more than the fraction of energy supplied to the engine calculated by Equ.(4.27). Since traditional explanations of thermal phenomena are based almost exclusively on the energy concept, these inventors ask why it should be forbidden to make use of a higher proportion of the energy supplied to an engine. Simply shaking one's finger at them and appealing to the "Second Law of Thermodynamics" that "forbids" their dream to come true does not seem to help. This is one of the problems we created for ourselves when we started conceptualizing heat as a form of energy. There is simply no simple way out of this seeming paradox in traditional representations of thermal phenomena.

[21] Note that the term *engine* is used for the central element of an entire thermal engine shown in Fig. 4.31, not for the complete system including the furnace and the cooler. Here, the engine is the part of the system that is designed to lower the entropy from high to low temperature and make use of the energy released in the fall of entropy.

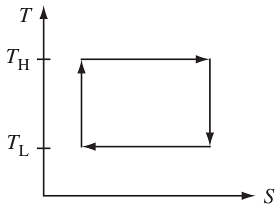

Figure 4.34: Carnot cycle in the *TS* diagram. It consists of four steps, two of them isothermal, the other two adiabatic. If the steps are performed ideally, i.e., if no entropy is produced in the agent, the cycle has the simple form of a rectangle. In the case of a Carnot heat pump, the cycle is traversed in the opposite direction (counterclockwise).

Carnot engines. The results derived in this section apply only to reversible devices and to what we might call *Carnot engines*. (There are reversible engines that are not Carnot engines, see Chapter 5.) An engine's task is to transport heat, i.e. entropy, from the furnace to the cooler. How can this be achieved? Consider, as Carnot did, an engine that absorbs entropy at *constant temperature* from a furnace. Then the absorbed entropy is lowered to the temperature of the cooler whereupon *all the entropy (heat)* is emitted, again at *constant temperature*. A heat engine operating in the manner described is called a *Carnot engine*. Actually, for us the *engine* is the working fluid employed, such as air or steam. The fluid operating in such an engine undergoes a cyclic process called a *Carnot cycle*, whose steps we can describe qualitatively in terms of the simple changes discussed in Section 4.3.3 (see Fig. 4.34). To be specific, let us assume the agent of the engine to be air. The first step in the cycle described above must be an isothermal expansion of the fluid. If air expands isothermally, it absorbs entropy at constant temperature. This is exactly what we want. Now the temperature of the air has to be lowered to the hotness of the cooler; this process has to take place without any heat being exchanged. Therefore this step must involve an adiabatic expansion. In other words, the air expands during the first two steps of the Carnot cycle.

Now the fluid has to emit the entropy it absorbed in the first step. Since the emission is to take place at constant temperature, this step must be an isothermal compression. In the end, we only have to return the agent to the starting point for it to be able to begin another cycle of operation. The final process is an adiabatic compression, which raises the temperature to the desired level, namely to the temperature of the furnace, without adding or removing entropy.

It might be instructive to quickly discuss the idea of a non-Carnot heat engine. Such a device absorbs and emits entropy at variable temperatures; most engines are designed in such a way that absorption and emission of entropy do not take place at constant temperature. If we call T_H the highest temperature during uptake of entropy, and T_L the lowest temperature during emission, the efficiency of an ideal heat engine is less than the Carnot figure, i.e., less than the famous factor $(T_H - T_L)/T_H$.

Dissipative heat engines. Real heat engines and heat pumps are dissipative. Entropy production can have several reasons, the main being heat transfer (we are going to discuss this in Section 4.6.3). We can neglect the actual sources of irreversibility for the moment and simply include a general source of entropy in an engine of the type depicted in Fig. 4.33; see Fig. 4.35. Adding entropy production to the model has important consequences. Some of the energy released in the fall of entropy from T_H to T_L will now be used for the process of producing entropy. The entropy resulting from dissipation must be emitted to the cooler and to the environment in addition to the entropy absorbed by the engine from the furnace. If we assume the temperature of the cooling process T_L to remain the same, the energy current to the environment will be larger than in the reversible case. This means that the energy available for the desired process is less than in a non-dissipative engine.

The real second law or first law efficiencies can be derived in analogy to Equ.(4.24) and Equ.(4.25). The equations that change are

$$\begin{aligned} 0 &= I_{S1} + I_{S2} + \Pi_S \\ 0 &= \mathcal{P}_{th} + \mathcal{P}_{el} + \mathcal{P}_{diss} \end{aligned}$$

It turns out that both efficiencies are reduced from their maximum values by amounts proportional to the ratio of entropy production to entropy absorbed from the furnace.

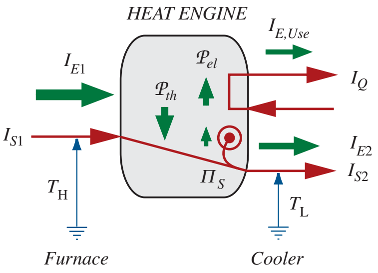

Figure 4.35: Process diagram of a dissipative heat engine. The difference between this and an ideal engine starts with an entropy production term. Adding this term changes all the quantities on the right side of the diagram. In particular, it reduces $\mathcal{P}_{el}$.

Available power and loss of power. The power of a fall of heat through a given temperature difference has been introduced in Equ.(4.20). It is often calculated with the temperature of the environment T_0 replacing the temperature of the cooler T_L. The power thus calculated is the maximum which can possibly be derived from a current of entropy emitted from a reservoir at temperature T in a given environment. For this reason it is called the *available power* $\mathcal{P}_{av}$ (or the *exergetic* power) of entropy:

$$\mathcal{P}_{av} = (T - T_0)I_S \tag{4.31}$$

Similarly, the loss of power due to irreversibility, i.e., as a consequence of entropy production, is expressed relative to the temperature of the environment T_0. The results introduced above show that there is a simple relation for the *loss of power* $\mathcal{L}$, i.e., the quantity by which the power of an engine is reduced relative to its maximum possible value for reversible operations:

$$\mathcal{L} = T_0 \Pi_S \tag{4.32}$$

Equ.(4.32) is simple to put into words, and simple to understand. If entropy is produced at a rate Π_S in an engine in an environment having temperature T_0, the entropy current from the device to the environment must be increased by Π_S. There is therefore an additional energy current to the environment, i.e., a loss, that is equal to $T_0\Pi_S$. This is what we call *lost power*.

Now we can understand why the Carnot efficiency, Equ.(4.27), is smaller than 1 (remember this is for an *ideal* engine). The power of the ideal engine is

$$\mathcal{P}_{el} = (T_H - T_L)I_S = (T_H - T_L)\Pi_{S,furnace} = I_{E1} - \mathcal{L}$$

i.e., it is smaller than the energy current supplied to the engine by the loss of power due to entropy production in the furnace.

4.4.4 Thermal Potential

When temperature and temperature scales were discussed in Section 4.3.1, the question was raised of whether any of them could represent a "true" thermodynamic temperature. If we take the conceptualization of the intensive thermal quantity seriously, the simplest meaning of "true" would be what we called *thermal potential*. The ideas of how entropy, temperature, and energy are related, and the results concerning engines can be used to make the concept of thermal potential more precise. Take the formula for the Carnot efficiency in Equ.(4.27). This quantity depends only upon temperatures. If we assume this measure of efficiency to have concrete meaning, if we want it to take a unique value for a concrete case of an engine, then the quantity in the formula—temperature—obtains meaning independent of special materials and processes. This leads to the concepts of *absolute temperature*, absolute in the sense of independent of a thermometric substance. It appears we can use the quantity T in our relations as a measure of the thermal potential.

There is commonly a second meaning to the word "absolute" in the term *absolute temperature*. We often mean that there is an absolute zero point of hotness. Entropy production and the Carnot efficiency both indicate that this must be so. Take Carnot's formula first. If T were not fixed on an absolute scale, results for the efficiency would depend upon the particular scale chosen.

The relation between the energy dissipated and the entropy produced could not be applied unambiguously either. Imagine there were negative temperatures, so Equ.(4.23) would predict negative entropy production rates which contradicts what we have been assuming. Fluidlike quantities that can be created and/or destroyed must have an absolute potential.[22]

For an entropy production rate to have an unambiguous meaning, the temperature must always be positive. Note that the relation between power, entropy production rate and (absolute) temperature, Equ.(4.23), tells us that the energy needed to produce one unit of entropy is the same as that needed to pump one unit of entropy from 0 K to the same temperature at which entropy that is produced appears in the world.

4.4.5 First and Second Laws of Thermodynamics

The presentation of thermodynamics in this chapter makes use of old forms of thought, namely, what we find in Sadi Carnot's work. However, it is not historical since it does not use the concepts and terms developed in traditional thermodynamics after 1850. Anyone who has learned some thermal physics before will wonder where I have been hiding the First and Second Laws of thermodynamics.

The First Law appears in a strongly generalized form as the law of balance of energy in Equ.(4.18) or Equ.(4.19). The traditional form of the First Law is the law of balance of energy for systems that exchange energy in thermal and mechanical processes. Since dynamical representations are rarely used, the presentation is in the form of an integrated balance: the change of energy of a system equals the energy exchanged in heating and cooling plus the energy exchanged mechanically. The first term (the energy of the system) is called *internal energy*, the energy exchanged in heating and cooling is called *heat*, and the third (energy exchanged mechanically) is called *work*. Thus, the traditional form reads: Change of internal energy equals heat plus work.[23]

The case of the Second Law of Thermodynamics is more intricate. In the literature, we

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[22] Take volume and pressure. Volume can be produced or destroyed by compression or expansion of a fluid, and pressure obviously has an absolute zero point.

[23] Some authors add a twist to this by using different signs for energy exchanged thermally and mechanically. We might say "heat added to a system" and "work done by the system." So the former term receives a positive sign in the First Law, the latter gets a minus sign.

find countless different forms of "the" Second Law in the introductory course. Needless to say, it is highly unlikely that all the forms express the same concepts and details, so we are left wondering what "the" Second Law actually is. The best that can be said is that the forms are variations of our law of balance of entropy (Section 4.3.2) or a relation between entropy, temperature and energy similar to Equ.(4.22), or combinations thereof.

For our purposes, it suffices to know that the First Law has something to do with energy balances, and the Second Law is somehow related to entropy. This explains the terms first law efficiency (Equ.(4.27)) and second law efficiency (Equ.(4.28)) of thermal engines.

QUESTIONS

29. How does the law of balance of energy change if thermal processes are included?
30. The Stirling engine in Fig. 4.10 is cooled by letting water from a faucet flow through the cooler of the engine. What happens to the operation of the engine if the flow of water is increased?
31. Why does the result of measurements for the power of a thermoelectric device (Fig. 4.11) suggest that thermal processes (in particular, the relation between thermal processes and energy) can be described in analogy to electric processes?
32. What are the units of entropy, entropy currents, entropy production rates?
33. How big does an entropy current flowing from a point at 500 K to one at 300 K have to be for the thermal power to measure 1.0 MW?
34. A typical nuclear power plant is a thermal engine running between an upper and a lower temperature of about 600 K and 300 K, respectively. What is the ideal thermal efficiency? The real thermal efficiency is more like 30%. What is the real second law efficiency in this case?
35. In what way are the relations for thermal power and for a thermal energy current related?
36. Why is it possible to conceptualize the production of entropy as a pumping of entropy from absolute zero temperature?
37. An immersion heater is operated at an electric power of 400 W. It has a temperature of 400 K. What is the entropy production rate in this heater? What are the entropy current and the energy current emitted by the heater in steady state?
38. To keep the interior of a home at 27°C in winter, the heating power of the heater is 6 kW. What is the entropy current leaving the home?
39. How are the thermal power and the useful power of an ideal heat engine related?
40. Why is the thermal efficiency of an ideal heat engine smaller than 1?
41. What is the *cop* of an ideal heat pump operated between 270 K and 300 K?
42. Real engines have efficiencies that are smaller than those of ideal ones. Why does this tell us that the entropy production rate must be non-negative?
43. Why should hotness have an absolute zero point?

EXAMPLE 4.4. The current of entropy through an ideal Carnot engine.

Consider a Carnot engine working between a furnace at 300°C and a cooler at 40°C. This ideal engine is known to have a mechanical power equivalent to 5.0 MW. (a) How large must the current of entropy through this engine be? (b) If the current of entropy is unchanged, how large must the temperature difference be for a power of 4.0 MW?

SOLUTION: (a) This is a direct application of the relation for the motive power of a heat engine. First we have to conclude that the thermal power of the engine is equal to its mechanical counterpart, namely 5.0 MW. The thermal levels, i.e. the temperatures, are given. Therefore:

$$|I_S| = \left|\frac{\mathcal{P}_{th}}{\Delta T}\right| = \frac{5.0}{573-313}\frac{\text{MW}}{\text{K}} = 19.2\cdot 10^3\,\frac{\text{Ct}}{\text{s}} = 19.2\cdot 10^3\,\frac{\text{W}}{\text{K}}$$

W/K (= Ct/s) is the SI unit of a current of entropy.

(b) The motive power depends linearly upon the difference of temperatures between the furnace and the cooler. For a power which is only 4/5 of the original one, it suffices to have a temperature difference equal to 80% of the original one, i.e. 208 K.

EXAMPLE 4.5. The current of entropy absorbed by a river cooling a thermal power plant.

It is known from the operation of a thermal power plant that the water of a river used for cooling carries away an energy current of 600 MW. (a) How large is the current of entropy entering the environment if the temperature of the water is taken to be equal to 27°C? (b) Express the entropy absorbed by a reservoir at constant temperature in terms of the energy exchanged in heating or cooling and the temperature, and (c) for the power plant given here calculate the entropy absorbed by the river in one day.

SOLUTION: (a) Assume the temperature of the water to remain constant. The amount of water used for cooling is so large that its temperature does not change very noticeably. In this case, the temperature remains constant and the current of entropy is given by

$$I_{S,in} = \frac{I_{E,th,in}}{T} = \frac{600\cdot 10^6}{(273+27)}\frac{\text{W}}{\text{K}} = 2.0\cdot 10^6\,\frac{\text{W}}{\text{K}}$$

The law relating currents of entropy and of energy describes an instantaneous situation. It is valid for any temperature, and for non-constant values as well. The currents will therefore generally change in time.

(b) Since the temperature of the water is constant during absorption of entropy, the amount exchanged can be computed easily according to Equ.(4.22):

$$W_{th} = T\int_{t_i}^{t_f} I_s dt = T\,S_e \quad\Rightarrow\quad S_e = \frac{W_{th}}{T}$$

Since entropy flows into the body of water at constant temperature, i.e., at a constant level, the energy exchanged is simply equal to the product of entropy exchanged and the temperature at which the exchange is taking place.

(c) The amount of energy exchanged in one day is equal to 600 MW · 86400 s = $5.2\cdot 10^{13}$ J, and the numerical value for the entropy exchanged is $5.2\cdot 10^{13}$ J / 300 K = $1.7\cdot 10^{11}$ Ct (Ct = J/K).

EXAMPLE 4.6. Energy dissipated in an immersion heater.

An immersion heater is placed in water and hooked up to a voltage of 110 V. The electric current is measured to be 1.5 A. How large is the rate of production of entropy in the heater and water combined if the temperature is 20°C? How much entropy is created in 10 s if the temperature changes linearly to 22°C during this period? The electrical quantities remain constant.

SOLUTION: The energy current given off by the heater is equal to

$$|I_{E,el}| = U|I_Q| = 165\,\text{W}$$

which is equal to the rate of dissipation of energy. Therefore:

$$\Pi_S = \frac{\mathcal{P}_{diss}}{T} = \frac{165}{273+20}\frac{\mathrm{W}}{\mathrm{K}} = 0.563\frac{\mathrm{W}}{\mathrm{K}}$$

The amount of entropy produced in this process is

$$\begin{aligned} S_{prod} &= \int_{0s}^{10s} \Pi_S dt \\ &= \int_{0s}^{10s} \frac{\mathcal{P}_{diss}}{T} dt = |I_{E,el}| \int_{0s}^{10s} \left[T_1 + (T_2 - T_1)\frac{t}{10\mathrm{s}} \right]^{-1} dt \end{aligned}$$

which is equal to

$$S_{prod} = 165\mathrm{W} \cdot 10\mathrm{s} \cdot \ln\left(\frac{T_2}{T_1}\right)(T_2 - T_1)^{-1} = 5.61\,\mathrm{J/K}$$

Since the temperature is almost constant, the result is very nearly equal to $\Pi_S \Delta t$, with a constant rate of generation of entropy.

EXAMPLE 4.7. A thermal power plant.

The thermal energy current due to burning of coal in a thermal power plant is 1.5 GW, while the mechanical energy current leaving the turbines is 0.6 GW. The steam driving the engine is emitted at a temperature of 50°C. If the turbines operate as an *ideal engine*, what are (a) the current of entropy flowing through the engine, (b) the temperature of the furnace, and (c) the Carnot efficiency?

SOLUTION: (a) The thermal energy current emitted with the steam is equal to the difference between the energy current entering the engine and the one driving the generator. In other words, it is 0.9 GW. At a temperature of (273 + 50) K, the current of entropy associated with this thermal energy flux is

$$I_S = \frac{I_{E,th,out}}{T_{\mathrm{L}}} = -2.79\frac{\mathrm{MW}}{\mathrm{K}}$$

(b) The temperature of the furnace can be calculated in terms of the currents of entropy and energy absorbed by the engine:

$$T_{\mathrm{H}} = \frac{I_{E,th,in}}{I_S} = 538\,\mathrm{K}$$

(c) According to Equ.(4.27), the Carnot efficiency is equal to

$$\eta_{\mathrm{I}} = \frac{538\mathrm{K} - 323\mathrm{K}}{538\mathrm{K}} = 0.40$$

The same result could also have been obtained with the help of the energy currents:

$$\eta_{\mathrm{I}} = \frac{I_{E,mech}}{I_{E,th,in}} = \frac{0.60}{1.50} = 0.40$$

Note that in these equations the magnitudes of the fluxes have been used. The second law efficiency is naturally equal to 1.0.

EXAMPLE 4.8. Heating water with a heat pump.

Assume that a heat pump has been installed that requires an energy current of 165 W for operation. The pump takes entropy out of the ground in winter for heating water. (The temperature of the ground is 2°C.) (a) How large is the entropy current at the beginning, with 20°C water? (b) How large is the current when the temperature of the water has reached 100°C? (c) How large are the energy currents entering the water in these two cases?

SOLUTION: (a) The current of entropy is calculated to be

$$I_{S,in} = \frac{I_{E,mech}}{T_H - T_L} = \frac{165\,\text{W}}{18\,\text{K}} = 9.17\frac{\text{W}}{\text{K}}$$

if the water has a temperature of 20°C.

(b) If the water has reached a temperature of 100°C, the current of entropy diminishes to 165 W/ 98 K = 1.68 W/K. With the same amount of energy, less entropy can be pumped through a larger temperature difference. (This result should be compared to the entropy current out of an immersion heater having a power of 165 W, which according to Example 4.6 is equal to 0.56 W/K at 20°C.)

(c) The energy current leaving the heat pump at 20°C (and entering the water) will be

$$\begin{aligned} I_{E,th,out} &= -\left(I_{E,mech} + I_{E,th,in}\right) = -\left(I_{E,mech} + T_L I_{S,in}\right) \\ &= -\left(165\,\text{W} + 275\,\text{K}\cdot 9.17\,\text{W/K}\right) = -2690\,\text{W} \end{aligned}$$

In the second case, it decreases to 627 W. Obviously, heating with an ideal heat pump must be more efficient than heating with an immersion heater.

EXAMPLE 4.9. The production of entropy in a non-ideal Carnot engine.

(a) For an engine with $\eta_I < \eta_C$, calculate the rate at which entropy is produced in the engine. Compute the numerical value for an engine operating between reservoirs at 600 K and 300 K, respectively, and which has an observed efficiency of 0.30. The thermal energy current entering the engine is 1.0 GW. (b) Show that there is a loss of available energy, and express the rate of loss in terms of the rate of production of entropy. How large is the loss for the engine described in (a) for one day?

SOLUTION: (a) In an engine which is operating in a steady state, the rate at which entropy is produced must be the difference between the rate at which entropy is emitted and the rate at which it is absorbed. Expressed more formally, according the law of balance of entropy Equ.(4.16) in the steady state ($dS/dt = 0$):

$$\Pi_S = -\left(I_{S,in} + I_{S,out}\right)$$

This equation can be transformed using the relations between currents of entropy and energy in heating. If we also use the expression for the efficiency of an ideal Carnot engine, Equ.(4.27), this changes to:

$$\begin{aligned} \Pi_S &= -\left(\frac{I_{E,th,in}}{T_H} + \frac{I_{E,th,out}}{T_L}\right) = -\left(-\left(1-\eta_I\right)\frac{1}{T_L} + \frac{1}{T_H}\right) I_{E,th,in} \\ &= \left(\left(1-\eta_I\right) - \frac{T_L}{T_H}\right)\frac{I_{E,th,in}}{T_L} \end{aligned}$$

or

$$\Pi_S = \left(\eta_C - \eta_{\mathrm{I}}\right)\frac{I_{E,th,in}}{T_{\mathrm{L}}}$$

If we introduce numerical values we obtain

$$\Pi_S = \left(0.50 - 0.30\right)\frac{1.0\,\mathrm{GW}}{300\,\mathrm{K}} = 0.67\,\frac{\mathrm{MW}}{\mathrm{K}}$$

The value of 0.5 is the Carnot efficiency of the engine operating between 600 K and 300 K. The rate at which entropy is absorbed is

$$I_{S,in} = \frac{1.0\,\mathrm{GW}}{600\,\mathrm{K}} = 1.7\,\frac{\mathrm{MW}}{\mathrm{K}}$$

which is 2.5 times larger than the rate of production.

(b) The loss of available power is the difference between the power available hypothetically and the actual mechanical power of the engine. According to the definition of the available power in Equ.(4.31), and the Carnot efficiency Equ.(4.27), we have:

$$|\mathcal{P}_{av}| - |I_{E,mech}| = \left(1 - \frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}\right)|I_{E,th,in}| - \eta_{\mathrm{I}}|I_{E,th,in}| = \left(\eta_C - \eta_{\mathrm{I}}\right)|I_{E,th,in}|$$

This can be expressed using the result obtained above:

$$|\mathcal{P}_{av}| - |I_{E,mech}| = T_{\mathrm{L}}\Pi_S$$

This result is important. It demonstrates that the loss of power due to dissipation is directly proportional to the production of entropy. At second glance, this is not so surprising. After all, the non-conservation of entropy leads to the loss in the first place. In one day, the loss is equal to 300 K · 0.67 MW/K · 86400 s = $1.74 \cdot 10^{13}$ J, which is equivalent to $4.8 \cdot 10^6$ kWh of energy. See Section 4.4.3 for an analysis of the loss of power and production of entropy.

EXAMPLE 4.10. Efficiency of a dissipative heat pump.

(a) Determine the coefficient of performance (*cop*) of a dissipative heat pump operating between the environment at temperature T_0 and a body to be heated at T. Show that it is smaller than that of an ideal pump. (b) Derive the relationship between the *cop* and the second law efficiency.

SOLUTION: (a) We start from the definition of the *cop* for heat pumps. It is the ratio of the heating power at temperature T and the mechanical power necessary for driving the pump. Taking into consideration the signs of the fluxes with respect to the pump we have:

$$\begin{aligned} cop &= \frac{-I_{E,th}(T)}{I_{E,mech}} = \frac{-I_{E,th}(T)}{-\left(\mathcal{P}_{av} - \mathcal{L}\right)} = \frac{-T\,I_S(T)}{-(T-T_0)I_S(T) + T_0\Pi_S} \\ &= \frac{T}{(T-T_0) - T_0\Pi_S / I_S(T)} < \frac{T}{T-T_0} \end{aligned}$$

The last expression is the *cop* of an ideal heat pump; it is clearly larger than the actual value.

(b) According to the definition of the second law efficiency, the actual *cop* must be equal to the product of the ideal *cop* and the second law efficiency:

$$cop = \frac{-I_{E,th}(T)}{I_{E,mech}} = \frac{\mathcal{P}_{av}}{I_{E,mech}} \frac{-I_{E,th}(T)}{\mathcal{P}_{av}} = \eta_{II} cop(ideal)$$

We could calculate the second law efficiency from the result for the *cop* given in (a). This must agree with the direct definition, which leads to:

$$\eta_{II} = \frac{\mathcal{P}_{av}}{I_{E,mech}} = \frac{\mathcal{P}_{av}}{\mathcal{P}_{av} - T_0 \Pi_S} = \frac{(T - T_0) I_S(T)}{(T - T_0) I_S(T) - T_0 \Pi_S} < 1$$

Note that the second law efficiency of a heat pump is the inverse of what we defined for a heat engine in Equ.(4.28).

4.5 ENTROPY-TEMPERATURE CHARACTERISTIC OF SIMPLE FLUIDS

So far, the discussion of thermal processes has centered upon generic relations such as the laws of balance of entropy and energy, and the properties of hotness. Results for engines were derived that depend only upon this type of relation, not upon details of materials used in actual devices. In this and the following sections, we will finally turn to some constitutive relations in their simplest forms. Still, the results will allow us to work on some interesting and real cases of thermal dynamical processes.

In this section we will discuss a common problem—the heating of solids and liquids—in a greatly simplified manner. We shall construct a model of a body of uniform temperature which is undergoing processes of heating. Indeed, heating and cooling are assumed to be the only phenomena which can be associated with such systems. Their volume will be assumed to remain constant. Therefore, in the simplest case, there will be only one independent variable—one function of time—which determines the properties of such a body. We can take this function to be the temperature $T(t)$. Other choices are possible, namely quantities which are related to and change with temperature. Obviously, these must be the entropy content and the energy of the system. A first question must be asked, namely, how temperature and entropy content of a body are related. We will answer it by introducing the *entropy capacitance*. Using the generic laws of balance of entropy and energy, we hope to find the solution of the problem posed, namely the functions $T(t)$, $S(t)$, and $E(t)$, and expressed in terms of these the flux and the rate of production of entropy.

4.5.1 The Model of Uniform Heating

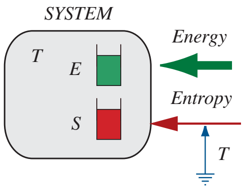

Figure 4.36: Process diagram of heating of a body: Entropy and Energy are added. If there are no other processes involved, the quantities added to the body are stored.

The model that will be constructed is one of uniform reversible heating or cooling. What this means is simple to express: When heated, a body receives entropy (and energy), but entropy may not be produced in the body as a consequence of this heating (Fig. 4.36). If this applies, and if it applies to cooling as well, entropy added to a body will be emitted in the reverse process. In between, it is stored in the system.

Is such a model realistic? In the Introduction, Section I.5, I discussed this question in some detail, so I can keep things short here. Commonly, entropy is produced when it spreads inside a body—we will understand this and be able to calculate entropy production rates for this process later in this chapter (Section 4.6). This means that we have to make assumptions as to the properties of the materials being heated. We need a material that lets heat (entropy) pass easily without producing any. A similar situation is called superconductivity in electricity. Charge flows without needing a driving force—an electric potential difference—and without producing entropy. Even though it is not correct, we apply this behavior to models of electric circuits where wires are treated as if they were superconductors. This is exactly what we are going to do for reversible heating and cooling. We assume that entropy can spread inside a body being heated without needing a temperature difference for the transport of entropy. Therefore, we have a condition of uniform reversible heating: A thermal superconductor having a single temperature throughout which stores the entropy it receives without producing any.

In real life, stirred liquids that are heated or cooled come close to this model. As examples will show, the model can be applied successfully to the dynamics of such materials. If the heater is placed somewhere in a liquid, stirring it will lead to an even distribution of the entropy. If the body cools through its surface, stirring ensures that the outer layers do not get colder than the inner ones. Naturally, solids do not heat or cool in this manner. However, if the solid has a relatively high conductivity for entropy, and if we are not interested in very short term behavior, we can still apply our model of uniform heating (for an example, see the heating of copper Fig. 4.1).

Balance of entropy and of energy. The model discussed here is represented symbolically by the process diagram in Fig. 4.36. If heating and cooling are reversible, the law of balance of entropy for the body takes the form

$$\dot{S} = I_S \tag{4.33}$$

(see Equ.(4.11)). Since heating and cooling are the only processes allowed, the balance of energy is

$$\dot{E} = I_{E,th} \tag{4.34}$$

The relation between entropy and energy fluxes in heating (Equ.(4.21)) let us combine these laws of balance. This leads to a relation between how the entropy and the energy of the simple materials discussed here change:

$$\dot{E} = T\,\dot{S} \tag{4.35}$$

This is an example of what is generally called a *Gibbs Fundamental Form*. We will encounter GFFs again and again in different applications throughout this book. Note that this is a relation between quantities describing a system—it does not contain any terms referring to processes such as fluxes or production rates.[24] If we want to recover processes from our model, we need to combine the laws of balance with the Gibbs fundamental form.

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[24] There are some aspects of the model presented here that need to be investigated in more detail, such as the use of time derivatives in the GFF, or the tacit assumption that the simple materials being heated go through reversible changes (this is part of the assumptions that led to Equ.(4.35)). These points will be discussed more fully in Chapter 5.

4.5.2 Adding Entropy to a Liquid

Consider electrical heating of water or ethylene glycol in an (almost) perfectly insulated container. This is achieved by thick insulation, but we also have to assume that inner layers of the container do not take up noticeable amounts of entropy. The electric heater produces entropy that is emitted to the liquid together with energy (Fig. 4.36). As a consequence, the temperature of the material changes.

The results of Section 4.4 allow us to determine the entropy produced and communicated to the liquid. To do so we need the electric power of the heater and the temperature of the water as functions of time. As in Example 4.6, the entropy production rate is calculated from the instantaneous values of dissipation rate and temperature, and the entropy production rate is integrated over time to obtain the (change of) entropy of the liquid. If we assume a certain value of entropy at a reference temperature, changes of entropy can be converted to entropy content. (In mechanical engineering, it is customary to set the entropy of materials equal to zero at 0°C.)

If we did the same experiment for 1 and 2 kg of a liquid, we would notice that the temperature rises more slowly in the second case (twice as slowly, to be precise). To make the results independent of the amount of the material and to get a temperature–entropy relation that is indicative of the material and not its amount, the measurements of the entropy of the body are referred to unit mass. This is called the *specific entropy s* of the material:

$$s = S/m \tag{4.36}$$

In this way, the temperature of the material is made a function of its specific entropy. The relation between specific entropy and temperature can be represented graphically as a *Ts*–diagram (Fig. 4.37), in a table, or by an analytical approximation.

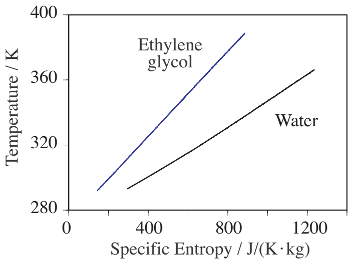

Figure 4.37: Experimental *Ts*-diagram of water and of ethylene glycol. The relation for glycol is almost linear, whereas the one for water resembles an exponential function. The entropy of the materials is arbitrarily set to zero at $T = 273$ K.

Experimental results for water and for ethylene glycol show two interesting features (Fig. 4.37). We need less entropy to make 1 kg of glycol warmer by 1 K than we need for water; and the shape of the temperature-specific-entropy or *Ts characteristic* of the materials is different. While it is close to being a linear function in the case of glycol, it is more of an exponential function for water.

4.5.3 Warming Factor and Entropy Capacitance

The meaning of the *Ts* characteristic for simple materials is analogous to that of a pressure-volume or voltage-charge characteristic of a tank or a capacitor, respectively (see

Section 1.4.2). Therefore, it can be described analogously to how this was done in hydraulics and electricity. The most significant feature of a material in the *Ts*-diagram is the slope of the $T(s)$ curve. It tells us how fast the temperature rises as a function of an increase in entropy. This slope is called the *warming factor* α_S (Fig. 4.38):

$$\dot{T} = \alpha_S \dot{s} \qquad \alpha_S = \frac{dT}{ds} \tag{4.37}$$

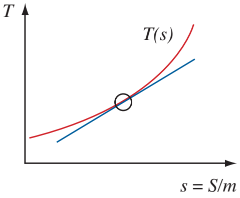

Figure 4.38: The slope of the *Ts*-relation tells us how easy it is to warm a body by heating.

The warming factor tells us how easy it is to warm a material; the larger the easier. Compare this to the definition of elastance of containers and fluids, or of capacitors. If $T(s)$ is a straight line in the *Ts*-diagram, the temperature can be calculated easily with the help of the warming factor:

$$T = T_{ref} + \alpha_S \left(s - s_{ref} \right) \tag{4.38}$$

Glycol is an example of a material having a constant warming factor which leads to the linear temperature–entropy characteristic demonstrated experimentally in the data of Fig. 4.37.

Entropy capacitance. The inverse of the warming factor is commonly used to represent the relation between temperature and entropy of a material. The inverse of the heating factor is called the *specific entropy capacitance* κ:

$$\dot{s} = \kappa \dot{T} \qquad \kappa = \frac{ds}{dT} \tag{4.39}$$

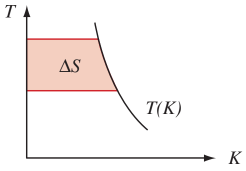

Figure 4.39: Temperature as a function of entropy capacitance. The diagram can be used to calculate the change of entropy of the body. The form of the diagram resembles that of a tank filled with entropy.

The *entropy capacitance*, $K = m\kappa$, has the usual meaning of a capacitance, as in hydraulics or electricity. In general, the entropy capacitance depends upon the temperature of the material. The change of entropy of a body can be calculated graphically from the temperature – capacitance diagram (Fig. 4.39).

4.5.4 The Energy of Simple Materials

It is common to introduce the *specific temperature coefficient of energy* (*specific heat*[25]) c which is calculated from the specific entropy capacitance by multiplying the latter by the temperature of the material ($c = T\kappa$). It allows us to directly determine the change of the energy of the simple materials discussed here (see the derivation below):

$$\dot{e} = c\dot{T} \tag{4.40}$$

where

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[25] The name specific heat (or specific heat capacity) is derived from the traditional usage in thermodynamics where a quantity of heat is measured in terms of energy. This usage is a remnant of the caloric theory in the thermodynamics formulated after 1850. Note that in the caloric theory, as in our conceptualization of thermal processes, the derivative of heat (caloric, entropy) with respect to temperature is a capacitance. The factor $c = Tds/dt$, however, is not.

$$c = T\kappa \tag{4.41}$$

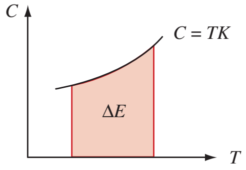

Figure 4.40: Temperature coefficient of energy (heat capacity) as a function of temperature, and energy change of a body.

Here, $e = E/m$, the energy per mass, is called the *specific energy* of the material. The specific heat of materials generally depends upon the temperature of the material. The change of energy of a body can be determined graphically from the specific heat – temperature diagram (Fig. 4.40).

Equ.(4.40) is derived simply from the balances of entropy and energy with the help of the relation between energy currents and entropy fluxes in heating, and Equ.(4.39):

$$\dot{E} = m\dot{e} = I_{E,th} = T\,I_S = T\,\dot{S} = Tm\kappa\dot{T}$$

It is quite common to report the values of specific heats of materials in tables and graphs. They are determined in the manner described above, by getting the temperature–entropy characteristic from which the entropy capacitance and the specific heat can be derived. Results for water (between 0°C and 100°C) and for some metals (down to 0 K) are shown in Fig. 4.41.

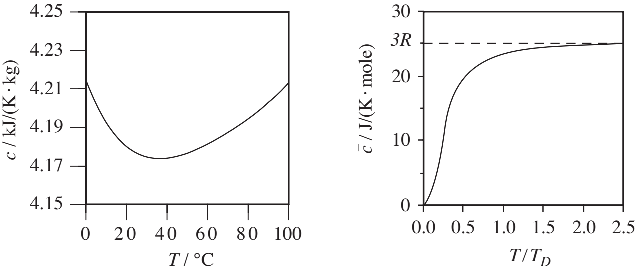

Figure 4.41: Left: Specific heat of water. Right: Molar specific heat $\bar{c} = T\bar{k}$, for several solids. At high temperatures, $\bar{c}$ reaches roughly $3R$ for most solids, where $R = 8.31$ J/(mole · K) is the universal gas constant. T_D is the Debye temperature which differs for different solids. (For copper and silicon the values are 343 K and 640 K, respectively.)

At high temperatures, which often mean room temperature or higher, c is a constant for solids. However, if we go to lower temperatures it becomes evident that c changes drastically. Specifically, at 0 K, entropy capacitances (and with them the values of c) become zero. This finding is equivalent to saying that it is impossible to reach 0 K in any experiment. Either statement is often called the *third law of thermodynamics*. In Fig. 4.41, values of c for some metals are shown. Table 4.7 lists values of κ and c for some liquids and solids for 20°C.

4.5.5 Materials With Constant Temperature Coefficient of Energy

Some materials (water, solids at high temperature) have almost constant specific heats. For these materials, entropy and energy can be calculated easily:

$$s = s_{ref} + c\,\ln\left(T/T_{ref}\right) \tag{4.42}$$

$$e = e_{ref} + c\left(T - T_{ref}\right) \tag{4.43}$$

The derivation of Equ.(4.42) follows from Equ.$(4.39)_1$ together with the definition of the temperature coefficient of energy $c = T\kappa$:

$$\dot{s} = \kappa \dot{T} = \frac{c}{T}\dot{T} \quad \Rightarrow \quad s(T) - s\left(T_{ref}\right) = \int_{t_0}^{t} \frac{c}{T}\dot{T}\,dt = c\int_{T_{ref}}^{T} \frac{1}{T}\,dT = c\ln\left(T/T_{ref}\right)$$

Equ.(4.43) is derived even more easily. All we have to do is integrate Equ.(4.40) for a constant value of the temperature coefficient c.

Now we can understand the form of the temperature – entropy characteristic of water which can be seen in Fig. 4.37. According to Equ.(4.42), the temperature T is an exponential function of the specific entropy s of water.

Table 4.7: Entropy capacitance and temperature coefficient of energy at 20°C

Substances	**Specific entropy capacitance** κ / J · K^{-2}kg^{-1}	**Molar entropy capacitance** $\bar{\kappa}$ / J · K^{-2}mole^{-1}	**Specific temperature coefficient of energy** c / J · K^{-1}kg^{-1}
Aluminum	3.06	0.0826	896
Concrete	2.87		840
Copper	1.31	0.0837	383
Glass (pyrex)	2.87		840
Granite	2.56		750
Ice (0°C)	7.69	0.123	2100
Iron	1.54	0.0864	452
Lead	0.44	0.0911	129
Lithium	1.16	0.0080	339
Sand (dry)	2.87		840
Silicon	2.40	0.0672	703
Sodium	4.16	0.0958	1220
Steel (average)	1.57		460
Wood (average)	8.53		2500
Mercury	0.47	0.0954	139
Petroleum	7.30		2140
Water	14.26	0.257	4180

4.5.6 Dynamical Models, Entropy, and Temperature

The temperature of a body is a central quantity in any dynamical model of a thermal system. It can be calculated from the entropy of the body in two steps, first by computing the specific entropy, and then by applying the temperature – entropy characteristic of the material. Alternatively, we can apply concrete relations of the type found in Equ.(4.38) or Equ.(4.42). The part of a dynamical model that calculates the temperature may look like the one shown in Fig. 4.42.

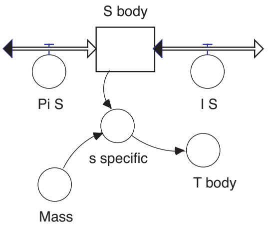

Figure 4.42: Diagram of a dynamical model for calculating the temperature of a body.

QUESTIONS

44. Why do we have to exclude compression or expansion from the model of heating or cooling of simple materials considered in this section?
45. Why is the warming factor of glycol constant? Does this mean that the entropy capacitance of glycol is constant as well?
46. The warming factor of glycol is about 0.13 K^2kg/J. What is its entropy capacitance?
47. What is the warming factor of a mixture of ice and water undergoing phase change?
48. Between 20°C and 30°C, the specific entropy capacitance of water is about 14 $J/(K^2kg)$. How much entropy has to be added to 10 kg of water to change its temperature from 20°C to 30°C? How much energy is added to the water at the same time?
49. Why does Fig. 4.40 tell us that for water $\Delta E = mc\Delta T$?
50. Consider the temperature – entropy characteristic of water in Fig. 4.37. Does the warming factor increase or decrease with temperature? What does this mean for the entropy capacitance of water?
51. How does the entropy capacitance of water depend upon temperature? How can this be derived from Equ.(4.42)?

EXAMPLE 4.11. Measuring the entropy capacitance of water.

Assume that two liters of water inside an insulated bottle are being heated by an immersion heater. The voltage and electrical current are kept constant at 220 V and 1.36 A, respectively. The temperature of the water is monitored. It is found that the temperature is quite nearly a linear function of time, with $dT/dt = 0.0356$ K/s. Determine $K(T)$ and $C(T)$, and calculate the entropy capacitance and the temperature coefficient of energy per mass for a temperature of 20°C.

SOLUTION: dT/dt is constant, with a value of 0.0356 K/s. The energy current is constant as well:

$$|I_{E,th}| = |U I_Q| = 299\,\mathrm{W}$$

Consequently, the temperature coefficient of energy is a constant (or nearly so) for water:

$$(TK)\dot{T} = |I_{E,th}|$$

The experimental results make $C = TK = 8400$ J/K for this body of water. The entropy capacitance of two liters of water is therefore equal to

$$K = \frac{8400\,\mathrm{J/K}}{T}$$

while the temperature coefficient of energy is constant and equal to $C = TK = 8400$ J/K. The entropy capacitance per unit mass at 20°C is $\kappa = 8400/(2 \cdot 293)\ \mathrm{J/(K^2 \cdot kg)} = 14.3\ \mathrm{J/(K^2 \cdot kg)}$. The temperature coefficient of energy per unit mass is $c = 8400/2\ \mathrm{J/(K \cdot kg)} = 4200\ \mathrm{J/(K \cdot kg)}$. Note that accurate measurements of the value of $c = T\kappa$ show that it is almost constant over the range of temperatures given (see Fig. 4.41, left).

EXAMPLE 4.12. The entropy of solids.

According to a constitutive law named after P. Debye, the molar entropy capacitance of a solid obeys the following relationship at very low temperatures:

$$\bar{\kappa}(T) = \frac{12\pi^4 R}{5T_D^3} T^2$$

Here, $\bar{\kappa}$ is the molar entropy capacitance (entropy capacitance per unit amount of substance n; see Chapter 6), and T_D is the Debye temperature. The temperature of the solid must be much smaller than this critical value for the formula to hold; i.e., $T \ll T_D$ (Fig. 4.41, right). (a) If the entropy of a solid is equal to zero at 0 K, how large is the entropy content of one mole of such a body at a temperature T? (b) What is the temperature coefficient of energy of this body?

SOLUTION: (a) According to Equ.(4.39) we obtain for the entropy content

$$S(T) = \int_0^T K\,dT = n\frac{12\pi^4 R}{5T_D^3}\int_0^T T^2\,dT = n\frac{12\pi^4 R}{15}\frac{T^3}{T_D^3}$$

Note that this quantity actually corresponds to the change of entropy content due to heating from absolute zero. In writing this we have set the entropy content equal to zero at 0 K.

(b) The temperature coefficient of energy is defined as the product of temperature and entropy capacitance. Therefore we have

$$C(T) = T\,K(T) = n\frac{12\pi^4 R}{5}\frac{T^3}{T_D^3}$$

EXAMPLE 4.13. The temperature coefficient of energy (specific heat) of glycol.

According to the data in Fig. 4.37, the temperature of glycol is nearly a linear function of the specific entropy given by

$$T = \alpha_S\left(s - s_{ref}\right) + T_{ref} \quad , \quad \alpha_S = 0.131\,\mathrm{K^2kg/J} \quad , \quad T_{ref} = 273\,\mathrm{K} \quad , \quad s_{ref} = 0\,\mathrm{J}/(\mathrm{K}\cdot\mathrm{kg})$$

Determine the specific entropy capacitance and the specific temperature coefficient of energy (specific heat) as functions of temperature for the range for which data has been taken.

SOLUTION: The specific entropy capacitance is the inverse of the warming factor α_S. Since α_S is constant, κ must be constant as well:

$$\kappa = 7.63\,\mathrm{J}/\left(\mathrm{K}^2\cdot\mathrm{kg}\right)$$

The temperature coefficient of energy is equal to the entropy capacitance multiplied by the (Kelvin) temperature. Thus:

$$c = 7.63\,\mathrm{J}/\left(\mathrm{K}^2\cdot\mathrm{kg}\right)T$$

Therefore, the specific heat c (specific temperature coefficient of energy) varies between 2240 J/(K·kg) at 20°C and 2850 J/(K·kg) at 100°C.

EXAMPLE 4.14. The time required to heat water using a heat pump.

Calculate the times needed to heat the same amount of water (a) using an ideal heat pump, and (b) using an immersion heater, if the electric power of both devices is the same.

SOLUTION: According to Equ.(4.34) and Equ.(4.40), the thermal energy current entering water during heating is proportional to the time rate of change of the temperature:

$$I_{E,th} = C\dot{T}$$

with C constant.

(a) Consider the energy current to be delivered by an ideal heat engine. According to Equ.(4.29), it is given by

$$I_{E,th} = \frac{T_{\mathrm{H}}}{T_{\mathrm{H}} - T_{\mathrm{L}}} I_{E,el}$$

If we combine this with the constitutive law stated above, we get the differential equation

$$C\dot{T} = \frac{T_{\mathrm{H}}}{T_{\mathrm{H}} - T_{\mathrm{L}}} I_{E,el}$$

The entropy delivered by the heat pump is taken out of the ground at constant lower temperature, while the upper temperature varies from the initial temperature $T_i \geq T_{\mathrm{L}}$ of the water to the final temperature T_f. Under these conditions, the solution of the differential equation delivers the time for heating using the heat pump:

$$t_p = \frac{C}{I_{E,el}}\left[T_f - T_i - T_{\mathrm{L}} \ln\left(\frac{T_f}{T_i}\right)\right]$$

(b) In the case of the immersion heater, the thermal energy current heating the water is equal to the electrical energy current of the immersion heater. Therefore the time required for heating is

$$t_{ih} = \frac{C}{I_{E,el}}\left(T_f - T_i\right)$$

This value is definitely larger than the one obtained for the heat pump.

EXAMPLE 4.15. The availability of a body of water.

Take a body of water of mass m at temperature T_i. How large is its availability in an environment at temperature T_0?

SOLUTION: The availability of a body is defined as the amount of energy which may be released by letting its entropy fall to the level of the environment. With the expression for the available power (Equ.(4.31)),

$$\mathcal{P}_{av} = \left(T(t) - T_0\right) I_S$$

and the balance of entropy and the definition of the entropy capacitance, we obtain

$$\mathcal{P}_{av} = -\left(T(t) - T_0\right)\frac{C}{T(t)}\dot{T}$$

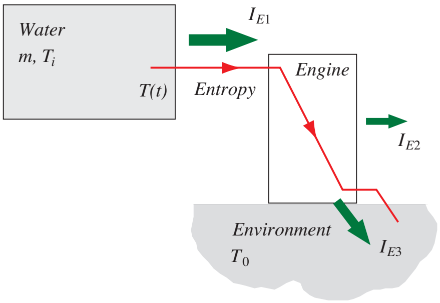

Figure Ex.15

The availability E_{av} is computed as follows:

$$E_{av} = \int_{t_i}^{t_f} \mathcal{P}_{av}\, dt = -\int_{t_i}^{t_f}\left(T(t) - T_0\right)\frac{C}{T(t)}\dot{T}\, dt = -\int_{T_i}^{T_a}\left(T(t) - T_0\right)\frac{C}{T(t)}\, dT$$

which leads to

$$E_{av} = mc\left[T_i - T_0 - T_0 \ln\left(\frac{T_i}{T_0}\right)\right]$$

This is how much energy can be released by an ideal heat engine from a body of water at temperature T_i in an environment at temperature T_0. The term proportional to $T_i - T_0$ is equal to the change of the energy of the body while the second term represents the energy emitted to the environment together with the entropy which has been withdrawn from the body. You can calculate the result directly by considering these integrated quantities. (See Example 4.16 for how to do this.)

EXAMPLE 4.16. Heat transfer (between two equal amounts of water) using a heat engine.

Consider two bodies having identical and constant temperature coefficients of energy C. Their initial temperatures are assumed to be T_1 and $T_2 < T_1$. Entropy is transferred from the hotter to the cooler reservoir using an ideal heat engine. What is the value of the final temperature attained by the bodies, and how much energy is given off by the heat engine in the mechanical process?

SOLUTION: In this case no entropy is produced, which means that the change of the entropy content of the two bodies is zero. Put differently:

$$\Delta S = \Delta S_1 + \Delta S_2 = 0$$

or

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_f} K\,dT + \int_{T_2}^{T_f} K\,dT = \int_{T_1}^{T_f} \frac{C}{T}dT + \int_{T_2}^{T_f} \frac{C}{T}dT\\ &= C\left[\ln\left(\frac{T_f}{T_1}\right) + \ln\left(\frac{T_f}{T_2}\right)\right] = C\ln\left(\frac{T_f^2}{T_1T_2}\right)\\ \Delta S &= 0\end{aligned}$$

which leads to

$$T_f = \sqrt{T_1T_2} \le \frac{1}{2}(T_1 + T_2)$$

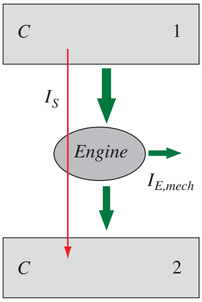

Figure Ex.16

The geometric mean is always smaller than or equal to the arithmetic mean. The energy released in the fall of entropy must be equal to the difference of the energy contents of the reservoirs at the beginning and at the end:

$$\begin{aligned}E_{mech} &= \Delta E_1 + \Delta E_2 = C\left(T_f - T_1\right) + C\left(T_f - T_2\right)\\ &= C\left[2\sqrt{T_1T_2} - \left(T_1 + T_2\right)\right]\end{aligned}$$

Since this quantity is negative, the bodies lose energy in the mechanical process.

EXAMPLE 4.17. Equilibrating temperatures in bodies in thermal contact.

Two bodies of water having equal mass and initial temperatures T_{1i} and T_{2i}, respectively, are brought in thermal contact. Otherwise, they are perfectly insulated from the environment. What is the final temperature reached, and how much entropy is produced in this process?

SOLUTION: Water is a substance having constant temperature coefficients of energy (specific heats). For two equal amounts, the *CT* diagram (Fig. 4.40, Fig. Ex.17) is the same horizontal line. Using the balance of energy on the entire process from beginning (*i*) to end (*f*), we see that

$$\Delta E = \Delta E_1 + \Delta E_2 = 0$$

$$C\left(T_f - T_{1i}\right) + C\left(T_f - T_{2i}\right) = 0$$

$$T_f = \frac{1}{2}\left(T_{1i} + T_{2i}\right)$$

which we can read off the *CT* diagram shown here. The associated *KT* diagram (Fig. 4.39, Fig. Ex.17) shows, that the change of entropy of the two bodies together is greater than zero: entropy has been produced:

$$\Delta S = \Delta S_1 + \Delta S_2 = C\left[\ln\left(\frac{T_f}{T_{1i}}\right) + \ln\left(\frac{T_f}{T_{2i}}\right)\right] = C\ln\left(\frac{T_f^2}{T_{1i}T_{2i}}\right)$$

$$= C\ln\left(\frac{\left(T_{1i} + T_{2i}\right)^2}{4T_{1i}T_{2i}}\right) > 0$$

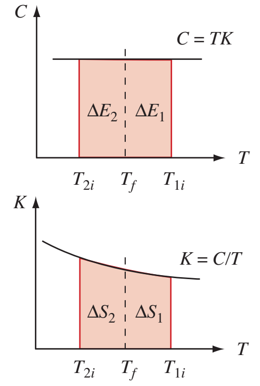

Figure Ex.17

4.6 ENTROPY TRANSFER IN HEATING AND COOLING

Now that we know how to calculate the temperature of simple materials if their entropy is known, we can turn our attention to the second main job of creating dynamical models of thermal systems: how to find expressions for entropy currents heating or cooling a body. In this section, overall heat transfer (entropy transfer) through layers separating a body from its environment, or two bodies in thermal contact, will be studied. A simple example of the former situation is a well stirred body of water inside a container in an environment (Fig. 4.4); the latter case is exemplified by two bodies of water separated by a thin wall, or a body such as a copper cylinder submerged in water of a different temperature (Fig. 4.1).

There are two main findings of this study. First, we will see that a simple expression for overall entropy transfer through layers can model realistic situation very well—we do not have to consider details to obtain some useful results. Second, and most importantly for our understanding of the dynamics of heat, we will recognize that heat transfer is dissipative, i.e., that entropy is produced when it flows through materials.

4.6.1 Thermal Driving Force and Overall Entropy Transfer

When entropy flows we normally speak of heat transfer. Entropy flows as the result of (1) spontaneous flow through matter due to a temperature difference, (2) convective transport with fluids, or (3) radiation. If one or all of these processes lead to a flow through a series of layers from a hot body to a colder body, we speak of overall entropy flow. The entropy flux I_S is expressed in terms of an *overall entropy conductance* G_S and the temperature difference (Fig. 4.43):

$$I_S = -G_S\left(T - T_a\right) \tag{4.44}$$

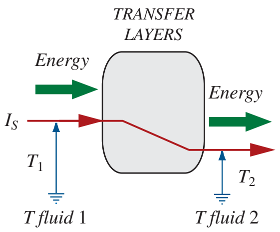

Figure 4.43: Entropy and energy transfer through layers from higher to lower temperature.

Here, T_a is the temperature of the environment of the body whose temperature is equal to *T*. The equation is written with respect to the body gaining or losing entropy. When we have identical conditions, but twice the surface area of transfer layers for entropy to flow through, the current doubles. Therefore, the conductance is written in terms the product of an *overall entropy transfer coefficient* h_S and the surface A through which the flow takes place:

$$I_S = -A h_S \left(T - T_a \right) \tag{4.45}$$

The entropy flux through a surface is related to its associated energy current by the temperature T at the surface of the body (Fig. 4.43):

$$I_{E,th} = -G_E \left(T - T_a \right) \tag{4.46}$$

$G_E = T G_S$ is called the overall *energy conductance*. The product of the entropy transfer coefficient and temperature,

$$h = T\, h_S \tag{4.47}$$

is called the *overall heat transfer coefficient*.[26] Therefore, the energy current accompanying the entropy flow is

$$I_{E,th} = -A h \left(T - T_a \right) \tag{4.48}$$

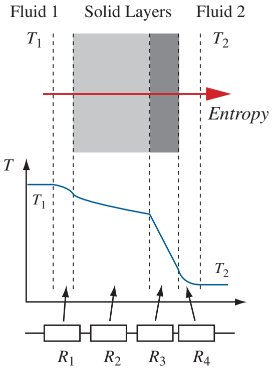

Figure 4.44: Entropy transfer through a series of layers. In each layer, the temperature drops (level diagram for temperature). Layers may be considered thermal resistors.

Thermal interfaces and transfer layers. What are heat transfer layers made of? What types of layers are there, and how might they be arranged? Most importantly, how can they be identified? The answer given here is preliminary and essentially qualitative. To understand details of transfer layers we need to study heat transfer in considerably more details. This we will do in Chapter 7.

Consider the case of the flow of heat through a wall of a building in winter. It is warm inside and cold outside, and there are two fluids (air) separated by solids. Clearly, the basic condition for the existence of a thermal interface between two bodies whose dynamics we are interested in, is a temperature difference from one side to the other of the layers that make up the interface.

So the wall—which may be made up of several different layers—must be warmer on the inside than on the outside. The temperature drops in the materials in the direction to the cold environment: There are *temperature gradients* in the layers (Fig. 4.44), and entropy is transferred by *conduction*. These gradients depend not only upon the overall temperature difference but upon the type of material a layer is constructed of as well.

This is not the whole story, though. When you touch the surface of the wall or window on the inside of the building, you may notice that it is cooler than the air of the room; measurements will confirm this impression. Clearly, there is a temperature drop from the inside air to the inside surface of the wall (Fig. 4.44). Since the air in the room is more or less well mixed, the temperature should be about the same throughout. However, in a thin layer near the solid interface, there is a so-called *convective transfer layer* (Fig. 4.45) in which the temperature changes in the direction of the flow of entropy.

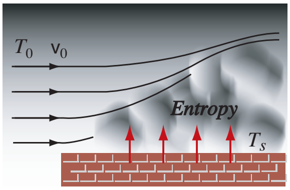

Figure 4.45: Entropy transfer from a solid body into a fluid (such as air or water) flowing past the solid surface.

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[26] Remember that the word *heat* has been used for energy transferred in heating or cooling since about 1850. That is why the term *heat* is associated with transfer coefficients for energy flowing with entropy.

The nature of entropy transfer through a convective layer is very complex. There is conduction immediately where the fluid touches the solid. The entropy transferred to the fluid is then carried away—how this happens depends upon the details of fluid flow in the transfer layer (Fig. 4.44). Simultaneously, radiation may contribute to the loss of entropy from a warm surface or a body. In practice, we often include the effects of radiation in a combined expression for the transfer at the surface of the solid interface. So, we should actually speak of a *convective-radiative transfer layer.*

Naturally, we expect a similar convective layer on the outside surface of the wall. Again, there is a temperature drop in the direction of the transfer. In summary, we can say that the temperature drops in several steps through a composite interface. There are several layers in series through which heat flows. And if we take into consideration different walls and windows simultaneously, we say that these are arranged in parallel. This sounds very much like the situation we might encounter in an electric circuit with conductive elements (resistors) combined in series and in parallel. Indeed, a particular layer in a heat transfer interface may be considered a *thermal resistor* (Fig. 4.44).

4.6.2 An Example of a Dynamical Model

As we have already seen in Section 4.2, combining this simple expression of an entropy current through a series of layers with the relation of entropy and temperature of a body, and the entropy balance for that body, leads to useful dynamical models for the cooling or heating of uniform bodies (Fig. 4.46). Here, I am going to add the details of entropy flow and storage discussed in this and the previous section to the model created in Fig. 4.16, and I will apply it to the examples of cooling and heating of a single body of water already discussed in Fig. 4.4 and in Section 4.2.

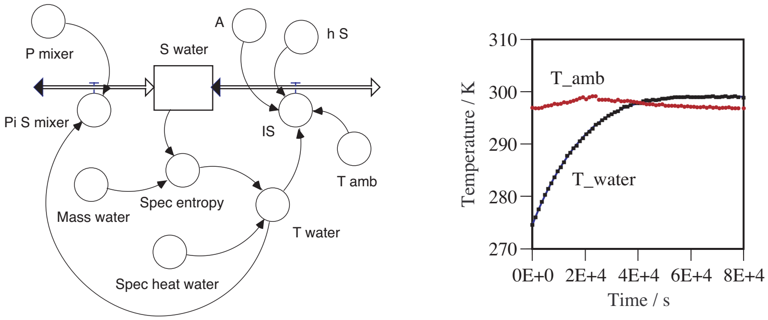


Figure 4.46: Left: SD model diagram of the cooling (or heating) of a uniform body at temperature *T*. Right: Application to the heating of cold water in a drinking bottle. The water is stirred, the aluminum bottle is inside an insulating bag. The simulation result (solid line) is barely visible since it fits measured water temperatures (dots) almost perfectly.

Take the concrete case of cold water in a drinking bottle sitting in a warm room. The water is stirred continuously. As always, we start with considering the balance of the relevant fluidlike quantity. Here it is the balance of entropy of the uniform body of water. Since there is a temperature difference between water and environment, entropy will flow; and since the water is stirred, there will be entropy produced inside the bottle. In summary, we have

$$\frac{dS_w}{dt} = I_S + \Pi_S \tag{4.49}$$

We need three constitutive laws to complete the model: (1) An expression for the relation between entropy and temperature of the system (body of water), (2) a relation for the entropy current expressed in terms of the temperature difference between inside and outside, and (3) the expression that relates entropy production and dissipation rate:

$$\begin{aligned} T &= T_{ref} \exp(s/c) \\ I_S &= -A h_S (T - T_a) \\ \Pi_S &= \mathcal{P}_{diss}/T \end{aligned} \tag{4.50}$$

The first relation derives from Equ.(4.42) with $T_{ref} = 273$ K and $s_{ref} = 0$ Ct/kg. The second was just introduced. For a specific case of the third relation, let me assume a process at constant mechanical (stirring) power. T_a is taken from experimental data reported in Fig. 4.46. The law of balance and the constitutive relations have been implemented in the system dynamics model in the same figure (Fig. 4.46, left). Simulation of the model and comparison with measured water temperatures lead to $\mathcal{P}_{diss} = 0.28$ W and $h_S = 0.0145$ W/(K^{2}m^2).

The exactly same model can be applied to the case of cooling of hot water in an uninsulated aluminum can (see also Section 4.2). In contrast to the slightly simplified model in Fig. 4.16, this one delivers even better results; there is virtually no difference between measured water temperatures and a simulation if we use $\mathcal{P}_{diss} = 1.7$ W, $h_S = 0.023$ W/(K^{2}m^2).

The difference between the entropy transfer coefficients is a consequence of the insulation used in the case of the cold water in the drinking bottle. In Chapter 7, we will study how to use the results of overall transfer coefficients and theory regarding different types of heat transfer through different layers to obtain material properties such as entropy conductivities or convective transfer coefficients. At this point it suffices to say that we understand why the overall entropy transfer coefficient of the case of the drinking bottle is smaller than that of the uninsulated can: In the former case, there is an additional layer for entropy to cross, so the flow will be smaller for the same temperature difference.

According to Equ.(4.47), the heat transfer coefficient is related to the entropy transfer coefficient by the temperature of the water. If we use an average value, we obtain $h = 7.6$ W/(K·m^2) for the case of the polished aluminum can. This value must represent the heat transfer from the surface of the can to the outside since transfer from water to metal and through the thin metal are much more efficient than transfer through the surface air layer. (When there are a few efficient layers and one bad one, the latter dominates the value of the entropy or heat transfer coefficients.) When we look in tables we find values of 12 – 14 W/(K·m^2) for heat transfer coefficients from surfaces to (still) air. The one measured in our experiment is considerably smaller. The reason for this will become clear in Chapter 7: In most situations, radiation from a surface adds to entropy transfer due to the direct contact of surface and air, making the transfer coefficient larger. The polished aluminum surface, however, is like a mirror which is a poor emitter for thermal radiation (Chapter 7).

An analytic model. The simplest models of cooling of bodies making use of particular material properties lead to an exponentially decreasing temperature. This happens, for example, in the case of a hot fluid in a can having constant values of entropy capacitance and entropy transfer coefficient, or in a model using constant energy related values (temperature coefficient of energy and heat transfer coefficient). In the latter case, the model equations are

$$\begin{aligned}&\frac{dS}{dt} = I_S \quad , \quad S(t=0) = S_0\\&\frac{dS}{dt} = K\frac{dT}{dt} = \frac{C}{T}\frac{dT}{dt}\\&I_S = -A\frac{h}{T}(T - T_a)\end{aligned}$$

with constant *C* and *h*. The second and third equations are inserted into the law of balance of entropy to yield

$$\begin{aligned}&\frac{C}{T}\frac{dT}{dt} = -A\frac{h}{T}(T - T_a)\\&\frac{dT}{dt} = -\frac{Ah}{C}(T - T_a) \quad , \quad T(t=0) = T_0\end{aligned}$$

The solution of this differential equation with its initial condition is

$$\begin{aligned}&T(t) = T_a + (T_0 - T_a)\exp(-t/\tau)\\&\tau = C/(Ah)\end{aligned} \qquad \textbf{(4.51)}$$

τ is the time constant of this system, and *Ah* may be considered a thermal resistance. This behavior is analogous to what we know from simple *RC* systems in fluids, electricity, or mechanics.

4.6.3 Uniform Bodies in Thermal Contact

Imagine two bodies of different temperatures in thermal contact. Entropy flows from the hotter to the colder, and temperatures equilibrate (Fig. 4.1). However, this is not the entire story. When entropy flows from a hotter to a colder body, more entropy is produced; this means that the entropy current increases in the direction of flow.

In common language, we would say that heat is produced when heat flows. The phenomenon is not as obvious as the production of heat in a fire or as a consequence of mechanical friction, but the conclusion is unavoidable. We can list many reasons that should convince us of the irreversibility of entropy transfer through a series of layers between bodies at different temperatures. For one, conduction of entropy is analogous to conduction of charge or momentum which are entropy producing processes. A thermal conductor is a *thermal resistor* just as an electric conductor has resistive properties. Secondly, real heat engines are not nearly as efficient as the formula for ideal ones would indicate. Their irreversibility is mostly due to heat transfer through the heat exchangers between furnace and working fluid, and fluid and cooler (mechanical and other operations in classical heat engines can be designed relatively close to ideal conditions).

Lost power in thermal conduction. The most convincing argument may be this. In the conduction of entropy through a thermally resistive material, energy is released as a consequence of the fall of entropy. There is thermal power accompanying the phenomenon (Fig. 4.47)—this is equal to the power of an ideal Carnot engine driven by the fall of entropy from T_1 to T_2. Energy released can drive another process. In a simple conductor that cannot undergo any other process (chemical, electrical, mechanical, etc.), the energy made available is completely dissipated—it is used to produce entropy. In the language of Section 4.4.3, we can speak of lost power:

$$\mathcal{L} = \left(T_1 - T_2\right) I_{S1}$$

On the other hand, the lost power is proportional to the entropy production rate and the temperature at which the entropy is emitted (here, this is T_2, see Fig. 4.47 and Equ.(4.32)):

$$\mathcal{L} = T_2 \Pi_S$$

Combining these expressions for lost power leads to

$$\Pi_S = \frac{1}{T_2}\left(T_1 - T_2\right) I_{S1} \tag{4.52}$$

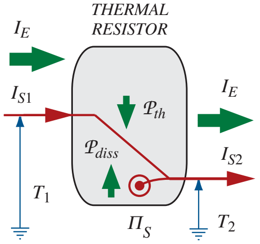


Figure 4.47: Entropy transfer due to a drop in temperature is dissipative: Entropy is produced as it flows.

Alternatively, this relation can be derived by combining the expressions for the balance of entropy and energy, and relations between energy and entropy currents. Note that the energy current passing through a series of transfer layers is constant in steady-state.

Entropy is always produced if entropy flows from a hotter to a colder place without driving another process. This effect has to be taken into account in dynamical models involving more than one body, i.e., as soon as we have two or more bodies in thermal contact whose thermal processes we want to understand.

Dynamical models of thermal capacitors and resistors. There appears to be an insurmountable obstacle to constructing simple dynamical models of entropy transfer between bodies at different temperatures. At least it seems that we cannot simply apply what we have already done, namely create models of spatially uniform dynamical systems. When entropy flows through bodies—specifically through solids—temperature changes from point to point, and so do the entropy currents. We will solve this problem later by producing continuum models (Chapter 13).

However, there is a simpler solution which combines ideas already used. Imagine two bodies of water which can be stirred to ensure homogeneous conditions. These bodies are separated by a solid wall through which entropy can flow. This system suggests a simple model: there are two spatially uniform bodies that store entropy and since they are supposed to be homogenous, let entropy pass easily. We have discussed this idea already: We may speak of thermal superconductors that store entropy—they are ideal *thermal capacitors*. These capacitors are joined by a thermal resistive element that conducts entropy as a consequence of a temperature difference but does not store entropy: The wall is a *thermal resistor*. A process diagram of this system is easily drawn; it explains in graphical terms what is meant by the model of uniform dynamical systems in thermal contact (Fig. 4.48). As the temperatures of the bodies of water equilibrate, this simple aggregate dynamical model produces the same amount of entropy as that calculated from the changes of state alone (see Example 4.17). Only, here we are able to follow the temperatures of the thermal capacitors in the course of time.

A possible representation of entropy production due to entropy transfer in a system dynamics model is shown in Fig. 4.49. The storage element in the middle is a symbol for the entropy of the transfer layer between the bodies. Since the transfer layer is a resistor, it does not store entropy. Therefore, the flow out of this element equals the sum of the flow into and the entropy production rate in the element:

$$I_{S2} = I_{S1} + \Pi_S \tag{4.53}$$

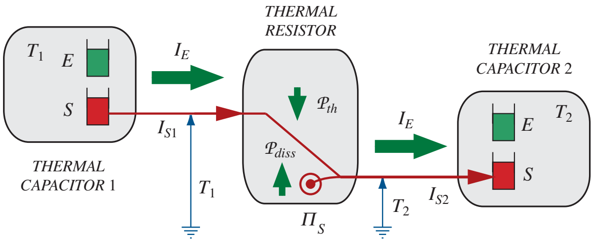


Figure 4.48: Model of two spatially uniform bodies in thermal contact. Processes in these bodies are assumed to be reversible. Irreversibility originates in the interface between the bodies.

This is equivalent to the junction rule known from electric or hydraulic circuits. If the model in Fig. 4.49 is applied to the equilibration of temperatures of two bodies of water that are perfectly insulated from the environment, we obtain very good results. If we were to neglect entropy production due to heat transfer, the computed final temperature would be noticeably too low.

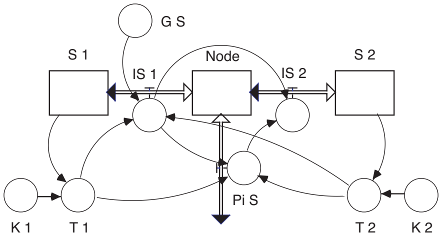


Figure 4.49: SD model diagram of heat transfer between two bodies. The transfer is dissipative. The central storage element serves as a node for the relation between entropy currents and entropy production rate.

4.6.4 Thermal Conductances for Composite Interfaces

The entropy conductance G_S is the factor describing entropy transfer through layers (Equ.(4.44)). An interface between two bodies in thermal contact may be thought of as a combination of conductors in series and in parallel (Fig. 4.50). If the conductances are independent of temperature, there are simple rules for combining them. In the case of two parallel layers between the same temperature difference, the combined conductance is

$$G_S = G_{S1} + G_{S2} \tag{4.54}$$

This is what we already know from electricity. The case of series connections is a little different because of the production of entropy in the elements (Fig. 4.50, bottom). With the relations used in this section and with a little algebra, we arrive at:

$$\frac{1}{G_S} = \frac{1}{G_{S1}} + \frac{T}{T_1}\frac{1}{G_{S2}} \tag{4.55}$$

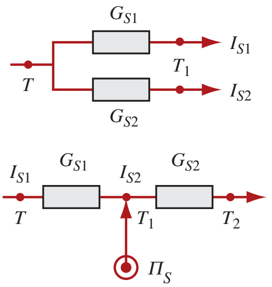


Figure 4.50: Parallel (top) and series (bottom) transfer layers.

The factor T/T_1 is different from the corresponding relation that applies to electric circuits; the difference is to be found in the fact that electric charge is conserved whereas entropy is not.

We could also write combinations of thermal (energy) conductances. Again, if they are independent of temperature, a relation analogous to Equ.(4.54) holds for parallel layers. The relation for layers stacked in series is simpler than Equ.(4.55); in fact, it takes the same form as in electricity, since the energy is conserved in its transit through transfer layers:

$$\frac{1}{G_E} = \frac{1}{G_{E1}} + \frac{1}{G_{E2}} \tag{4.56}$$

It is not possible for entropy conductances and energy conductances to be both independent of temperature. In real life, neither quantity will be constant. Still, either one of the assumptions—constant G_S or constant G_E—will suffice for many applications. Finding the one that delivers better results is a matter of trying them out.

Questions

52. What observations suggest that entropy currents through a heat transfer layer might be proportional to the temperature difference across the layer?
53. Why is heat transfer an entropy producing process?
54. Entropy flows through a layer from 600 K on the hot side to 300 K on the cold side. By what fraction does the entropy current increase?
55. Why does Equ.(4.53) apply to an entropy junction (node)?
56. For a given entropy current through a temperature difference, does the rate of entropy production only depend upon the temperature difference or does it matter at what level the temperatures actually are?
57. Why is the relation for combining conductances for transfer layers in series different from the form known to apply to electric circuits?

EXAMPLE 4.18. Response of a temperature probe to changing environments.

A temperature sensor is in air at room temperature. It is suddenly put into hot water. After the temperature reading has stabilized, it is taken out of the water, dried, and left lying in air at room temperature (data of process is shown in the diagrams of Fig. Ex.18.1; an enlargements of the initial rise is seen in the diagram on the right).

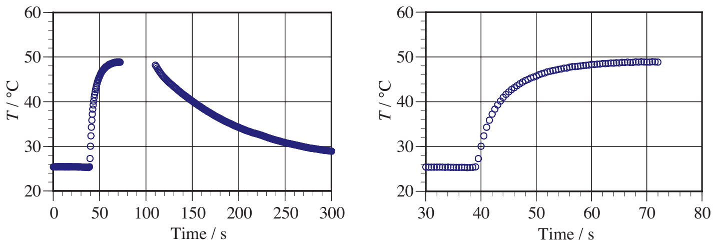
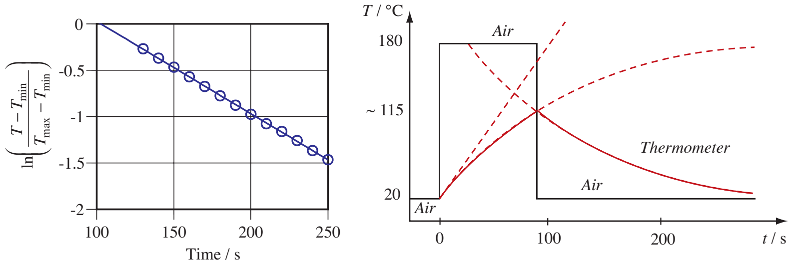


Figure Ex.18.1

(a) Determine the time constant by hand (without transforming the graph) for the temperature sensor in water. How could you do this most easily? What is the time constant? (b) Create a graph from the temperature data for the equilibration in air (after 120 s) in which the temperature might most likely be a linear function. Use this diagram to determine the time constant of the thermometer in air. What is the value of this time constant? (c) Assume the heat transfer coefficient from the thermometer (steel) to air to be about 14 W/(K·m^2). How large is the heat transfer coefficient from water to the thermometer? (d) The thermometer is taken from the kitchen at 20°C and placed into an oven at 180°C for 1.5 minutes. Then it is placed in the kitchen again. Sketch the expected behavior of the temperature reading as a function of time (use numerical values where necessary and possible).

SOLUTION: (a) The time constant corresponds to the time it takes for the temperature to rise to 63% of the initial temperature difference. This difference is 49°C – 25.5°C = 23.5 K. 63% of this is 15 K. Therefore, after one time constant, a temperature of 25.5°C + 15°C = 40.5°C should be reached. We can simply count the points in the diagram in Fig. Ex.18.1 (right). After about 10 data points, the temperature is a little above 40°C. Therefore, the estimate of the time constant for the thermometer in water is 5.0 s.

Figure Ex.18.2



(b) We prepare a graph for the decreasing temperature with a logarithmic scale for the temperature. This can be done by using the (relative) difference of the temperature of the thermometer and the surrounding air:

$$y = \ln\left(\frac{T - T_{min}}{T_{max} - T_{min}}\right)$$

We expect $T(t)$ to be an exponentially decaying function:

$$T = T_{min} + \left(T_{max} - T_{min}\right)\exp\left(-(t - 100)/\tau\right) \quad \Rightarrow \quad \ln\left(\frac{T - T_{min}}{T_{max} - T_{min}}\right) = -\frac{t - 100}{\tau}$$

The slope of the logarithmic relation in Fig. Ex.18.2 is 0.010 s^{-1}, so $\tau = 100$ s.

(c) If we take as the dynamical model of the thermometer a uniform body having a certain entropy resistance from its surface to the environment, and having a certain entropy capacitance, the time constant of the system must then be

$$\tau = R_S K$$

Since K is the same for both phases of the process, the entropy resistance from water to thermometer must be 100/5.0 = 20 times smaller than that for air to thermometer. Therefore, the conductance must be 20 times larger. This applies to the energy conductance as well, or to the energy transfer coefficient. Therefore, $h = 20 \cdot 14$ W/(K·m^2) = 280 W/(K·m^2) for the transition from thermometer to air.

(d) For the dynamics of the thermometer, the behavior in air is required. The thermometer reacts to a sudden temperature change with a time constant of 100 s. Therefore we should have a response like the one constructed in the diagram on the right of Fig. Ex.18.2.

EXAMPLE 4.19. Heating a home and estimating entropy production in heat transfer.

Consider a home having a thermal conductance of 300 W/K to be heated in winter. In steady state, temperatures are 20°C and 0°C on the inside and the outside, respectively. (a) Estimate the entropy conductance of the home and the entropy current leaving the home. (b) If the radiators supplying the entropy are to have a surface temperature not exceeding 60°C, what must their surface area be? (The heat transfer coefficient from their surfaces to the air in the rooms is 14 W/(K·m^2). (c) What is the relative error made in calculating entropy currents (from the radiators to the rooms, from the rooms to the outside environment) if entropy production due to transfer is neglected?

SOLUTION: (a) Entropy conductance and thermal (energy) conductance are directly related by temperature. If we take the temperature of the inside of the home, we have

$$G_S = \frac{1}{T_i} G_E = \frac{1}{293} 300 \frac{\mathrm{W}}{\mathrm{K}^2} \approx 1 \frac{\mathrm{W}}{\mathrm{K}^2}$$

This leads to an entropy current of

$$I_S = G_S \left(T_i - T_a\right) = 1 \cdot 20 \frac{\mathrm{W}}{\mathrm{K}} = 20 \frac{\mathrm{W}}{\mathrm{K}}$$

leaving the inside of the home. The associated energy current is roughly equal to 300 K · 20 W/K = 6000 W.

(b) According to Equ.(4.45), the entropy current from the radiators into the rooms is related to the temperature difference between radiators and rooms, the entropy transfer coefficient, and the surface area through which the current enters the space inside the home. If we assume the entropy current leaving the home to be equal to the one coming from the radiators, we have:

$$I_S = A h_S \left(T_r - T_i\right) \quad \Rightarrow \quad A = \frac{I_S}{h_S\left(T_r - T_i\right)} = \frac{I_S}{h/T_r \left(T_r - T_i\right)} = \frac{20 \cdot \left(273 + 60\right)}{14 \cdot \left(60 - 20\right)} \mathrm{m}^2 = 12 \mathrm{m}^2$$

(c) First, take the case of radiators and rooms. The entropy current entering the room is greater than the one leaving the radiators by the entropy production rate. The relative value of the error is

$$\frac{\Pi_S}{I_S} = \frac{T_r - T_i}{T_i} \approx \frac{40}{300} \approx 0.13$$

(see Equ.(4.52); this means that we have overestimated the surface area of the radiators in (b) by about 10%). The corresponding relative error for entropy transfer from the home to the environment is 0.07.

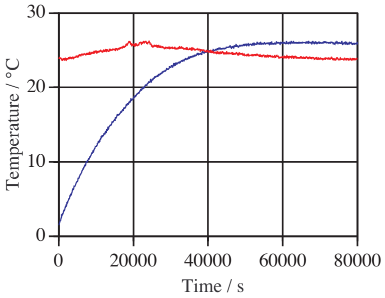
EXAMPLE 4.20. Conductors in series.

Very cold water is filled into an insulated aluminum bottle which is then sealed. The bottle is allowed to stand in a warm room for about one day. The water is constantly stirred by a magnetic stirrer. In the diagram (Fig. Ex.19) one sees the temperatures of both the water and the environment.

Use the experimental results to estimate the missing parameters of a model of the processes undergone by the water (power of the stirrer and overall entropy transfer coefficient). Use this to estimate the entropy transfer coefficient of the insulation.

Information: Height of the container: 15 cm, inner radius: 3.5 cm, thickness of the aluminum: very thin, thickness of the insulation: 6 mm. The lid and the bottom are perfectly insulated. The inner heat transfer coefficient from the water to the container is very high. The outer one from the insulation to the air is 12 W/(K · m^2). Treat the insulation as a flat layer.

Figure Ex.19



SOLUTION: The law of balance of entropy of the body of water includes the transfer of entropy from the environment and the entropy production rate:

$$\dot{S} = I_S + \Pi_S$$

The rate of change of entropy can be related to the rate of change of the temperature of the body of water:

$$\dot{S} = K\dot{T}$$

The entropy capacitance can be calculated from the specific entropy capacitance and the mass of the body of water which is equal to $0.15 \cdot \pi \cdot 0.035^2 \cdot 1000$ kg = 0.58 kg. Therefore, we find $K = 14 \cdot 0.58$ J/K^2 = 8.1 J/K^2.

Entropy current and entropy production rate are expressed by

$$I_S = G_{S,total}\left(T_a - T\right) \quad , \quad \Pi_S = \mathcal{P}_{mech}/T$$

If we take two pieces of data from the experiment, the missing parameters can be determined. A first one can be obtained from conditions at $t = 0$ s:

$$K\dot{T} = G_{S,total}\left(T_a - T\right) + \mathcal{P}_{mech}/T$$
$$8.1 \cdot 1.38 \cdot 10^{-3} = G_{S,total}\left(24 - 2\right) + \mathcal{P}_{mech}/275$$

The rate of change of temperature at $t = 0$ s can be estimated graphically, and so can the relevant temperatures. For large times around 80,000 s we have

$$0 = G_{S,total}\left(T_a - T\right) + \mathcal{P}_{mech}/T$$
$$0 = G_{S,total}\left(26 - 23.8\right) + \mathcal{P}_{mech}/299$$

For steady-state, the rate of change of entropy equals zero. Temperatures have again to be taken from the experimental results. Now there are two linear equations for G and $\mathcal{P}$ which turn out to be equal to $4.6 \cdot 10^{-4}$ W/K^2 and 0.30 W, respectively. The entropy transfer coefficient turns out to be equal to $4.6 \cdot 10^{-4}$ W/K^2 / $(2\pi \cdot 0.035 \cdot 0.15)$ m^2 = 0.014 W/(K$^2 \cdot$ m^2) (compare these results to the ones obtained from the dynamical model in Section 4.6.2).

The entropy transfer coefficient for the insulation alone is obtained as follows. Since the temperatures involved are not very different, we can simply add the inverse values of the conductances to obtain the inverse of the total conductance (Equ.(4.55)). Since the surface is (nearly) the same everywhere, this also holds for entropy transfer coefficients. Therefore, 1/0.014 = 1/G_S + 1/(14/295), or G_S = 0.020 W/(K$^2 \cdot$ m^2).

EXAMPLE 4.21. Laws of balance of entropy in a model of equilibration.

Consider the experiment shown in Fig. 4.1. A copper block is submerged in water which is inside a jar made of glass. The jar is insulated from the environment, but the insulation is not perfect. Formulate all relevant laws of balance of entropy for a dynamical model of this system. Treat glass, water, and copper as three uniform bodies.

SOLUTION: There are three entropy storage elements (copper: c, water: w, glass: g) and two entropy transfer interfaces (between c and w, and w and g, respectively). The entropy transfer layers between glass and environment need not be included in the model. Combining these assumptions leads to a model diagram of the form shown in Fig. Ex.21.

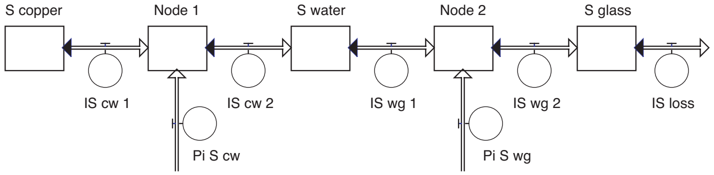


Figure Ex.21

The laws of balance of entropy for the storage elements are:

$$\frac{dS_c}{dt} = -I_{S,cw1}$$
$$\frac{dS_w}{dt} = I_{S,cw2} - I_{S,wg1}$$
$$\frac{dS_g}{dt} = I_{S,wg2} - I_{S,loss}$$

For the transfer layers they take the form of junction rules (Equ.(4.53)):

$$I_{S,cw2} = I_{S,cw1} + \Pi_{S,cw}$$
$$I_{S,wg2} = I_{S,wg1} + \Pi_{S,wg}$$

Note that laws of balance do not include constitutive information concerning flows etc.

4.7 THERMAL ENGINES AND HEAT TRANSFER

Thermal engines in general, and heat engines in particular, do not work reversibly. There are many reasons for concrete irreversibilities, i.e., for entropy production. If we disregard the origin of the entropy that drives the engine, the most important entropy producing processes are friction and heat transfer, and among these heat transfer dominates in a typical heat engine.

In this section, a simple model of a Carnot engine with heat transfers through sizeable temperature differences will be created. This prepares the ground for an interesting idea we will take up again in detail in Chapter 9, namely that processes should be designed in such a way that they minimize entropy production. Since entropy production in an engine means loss, this idea is certainly not farfetched. Then, thermoelectric devices will be modeled. We have advanced to a point in the theory of dynamical thermal processes where we can discuss in a rather simple manner a phenomenon that is commonly considered difficult to understand and model.

4.7.1 A Carnot Engine Between Heat Exchangers

The central part of a heat engine—the working fluid—operates by lowering entropy from a high to a low temperature. As we will see, the entropy transfer to and from this part of the engine is the source of the greatest irreversibility. Let us consider a Carnot engine, i.e., a device that receives entropy at *constant* high temperature T_{1E} (Fig. 4.51) and gives it up at *constant* low temperature T_{2E} (the index E denotes the actual engine). The lowering of the temperature of the working fluid—and therefore the lowering of the entropy from T_{1E} to T_{2E}—is the result of expansion of the gas in the engine. If we assume, as is fairly reasonable, that the mechanical operations in the engine are reversible, the core of the thermal system operates reversibly.

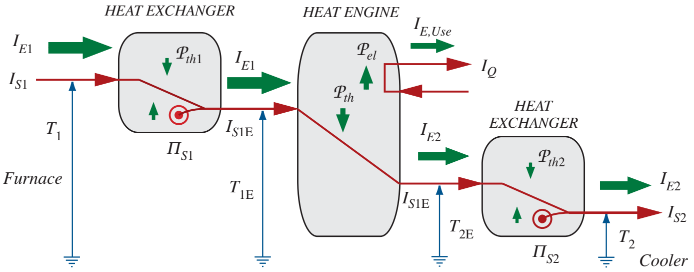


Figure 4.51: Process diagram of a reversible engine sandwiched between two heat exchangers. The heat exchangers make it possible for entropy to be transferred at finite rates, but they cause entropy production and loss of power.

Now we have to take a close look at how entropy enters and leaves the reversible engine. Clearly, entropy comes from the furnace and goes to the cooler (Fig. 4.51). If we want heat transfer to happen in finite time, there need to be temperature differences across the heat exchangers that facilitate the flow of entropy to and from the engine. A zero temperature difference—which would be ideal for the engine so it could utilize the entire temperature range from T_1 to T_2 (Fig. 4.51)—leads to entropy currents that are zero. Completely perfect engines would simply not run.

If there are temperature differences that allow the engine to run at realistic speeds, there will necessarily be entropy production and, in the end, loss of power. This loss can be quantified by adding the entropy production rates in the heat exchangers and multiplying this sum by the lowest temperature of the system:

$$\mathcal{L} = T_2\left(\Pi_{S1} + \Pi_{S2}\right) \tag{4.57}$$

Heat exchangers. The process diagram in Fig. 4.51 demonstrates, in a strongly simplified manner, how we can understand the function of actual heat exchangers. According to this model, they are nothing but a heat transfer interface between two bodies at different temperatures. Entropy flows through them, which causes more entropy to be produced. The transfer rate (current) depends upon the temperature difference across the exchanger and the heat transfer properties quantified by the entropy conductance of the device. The theory of heat exchangers according to this model is contained in the equations presented in Section 4.6. If we combine this theory with what we know about reversible engines, the model in Fig. 4.51 can be quantified.

An optimal endoreversible engine. As mentioned above, the main contribution of entropy production stems from heat transfer which takes place during heating and cooling of the working fluid. To effect this heating and cooling, heat exchangers are added between the furnace and the fluid, and between the fluid and the cooler. In the simplest model of this kind, the fluid is assumed to operate reversibly. All irreversibilities take place in the heat exchangers (Fig. 4.51). Such a model engine is called *endoreversible*.

With T_1, T_2, and I_{S1} held fixed, the model can be optimized (see Chapter 9) by determining the condition of minimal entropy production rate (which coincides with maximum useful energy current). This leads to the so-called Curzon-Ahlborn efficiency:[27]

$$\eta_{1,CA} = 1 - \sqrt{T_2/T_1} \tag{4.58}$$

This is a much more realistic estimate of the actual efficiency than the Carnot efficiency derived in Equ.(4.27). It will be derived in Chapter 9, together with several other interesting applications of the concept of minimization of entropy production. To see how well it works, take the example of a large nuclear power plant. Data shows a thermal (first law) efficiency of 30% with upper and lower temperatures for the system of 300°C and 30°C. The Curzon-Ahlborn estimate yields a value of 28%. Compare this to a value of 47% obtained from Carnot's formula.

4.7.2 Thermoelectric Generators and Coolers

Thermoelectricity provides a beautiful example of thermal engines coupled with entropy transfer. The theory of thermoelectric effects is commonly considered an advanced topic, but you will see that we already know enough to produce a dynamical model of thermoelectric devices. It will provide an understanding of the overall function of a complete device without regard to material details of the processes (a brief description of the structure of thermocouples is given in Section 4.7.3). A more detailed study of thermoelectricity will be undertaken in Chapter 13.

Observations. Two observations regarding thermoelectricity let us understand the basic aspects of the phenomenon. First, if we place a thermoelectric device—a Peltier device as in Fig. 4.11—between two bodies at different temperatures, it operates as an electric generator that can drive an engine. Temperature differences produce a voltage (an open circuit voltage, if we do not connect a load). Observation shows that the open circuit voltage—the thermoelectric voltage U_{TE}—grows in proportion to the temperature difference across the device:

$$U_{TE} = \varepsilon(T_2 - T_1) \tag{4.59}$$

The coupling factor ε in this relation is called the *Seebeck coefficient*. U_{TE} can be viewed as the "electromotive force" as in a battery. In this case, chemical reactions are responsible for this voltage. Here, the temperature difference causes a conductive flow of entropy through the device from hot to cold which somehow must lead to an electric

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[27] The type of heat engine called *endoreversible* was first proposed and analyzed by Curzon and Ahlborn (1975). They calculated the power of the engine and determined the condition for its maximum. The efficiency at maximum power, Equ.(4.58), has since been called the Curzon-Ahlborn efficiency. A simpler derivation was given by DeVos (1985). The problem was later investigated from the point of view of the minimization of the production of entropy (Salamon et al., 1980; Andresen et al., 1984).

effect. This suggests that the thermoelectric effect is the result of a coupling of transports of entropy and of charge: As entropy flows through the device, charge is swept along leading to an electric field and a voltage. When the circuit is open, the flow of charge will stop and a certain voltage will have been established; this is U_{TE}. Remember that the voltage measured at the terminals will be different from the open circuit voltage if charge flows through the generator (see Equ.(4.63) further below).

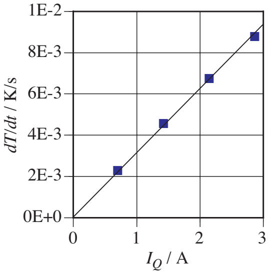

Figure 4.52: Rate of change of temperature of the cold body of water shown in Fig. 4.8, as a function of the electric current through the Peltier device for $\Delta T = 0$ K. The rate of change of temperature is proportional to the entropy current withdrawn from the body of water.

The second observation confirms this basic idea. We can operate the Peltier device as a heat pump by driving it electrically. This means that we force an electric current through the element that leads to a flow of entropy in the direction opposite to its spontaneous flow. In other words, entropy is pumped. Consider the special case of starting the pumping of entropy when the temperature difference across the device is zero—so there is no conductive entropy current from hot to cold. Experiments show that the entropy current coupled to the charge current ($I_{S,TE}$) grows proportionally to the flow of charge (Fig. 4.52):

$$I_{S,TE} = \alpha I_Q \tag{4.60}$$

The coupling factor α is called the *Peltier coefficient*. It turns out that Seebeck and Peltier coefficients must be equal:

$$\alpha = \varepsilon \tag{4.61}$$

If they were not equal, the energy principle for the thermoelectric processes taking place would be violated. The validity of this statement will be demonstrated further below when we take a look at the power of thermoelectric devices.

Seebeck and Peltier coefficients can be positive or negative. The sign depends upon the sign of the charge being swept along with entropy through the conductor.

Dynamical model of a Peltier device. The observations discussed above concern the "pure" effects: thermoelectric voltage at zero electric current, and entropy pumped at zero temperature difference. In general, the special conditions will not hold and we have to deal with the conductive effects of the flows of entropy and charge as well. To understand this better, let us construct the simple dynamical model I have been mentioning. The starting point is the simple observation that under general conditions, a Peltier device looks like a panel having a hot and a cold side. At the same time, it has a side that is at high electric potential and one that is at lower potential. This suggests the following model. The device consists of two entropy storage elements (for the cold side and the hot side, respectively; entropy stored in bodies makes them warm), and two electric capacitors (for the high potential and the low potential, respectively; the charge of a capacitor leads to its electric potential).

A graphical representation of these ideas is presented in Fig. 4.53. Between the electric capacitors we have an electric generator responsible for U_{TE} and resistor for the conductive transport of charge—just like in a battery. Between the thermal capacitors there is a thermal resistor for the conductive flow of entropy from hot to cold. The coupled flows of entropy and charge that are responsible for the thermoelectric effect are like a bypass to this thermal resistor. There is a non-dissipative transport of entropy that is directly coupled to the electric current.

This model lets us construct the general equations for entropy transport through and voltage across the thermoelectric device. If there is no conductive transport of entropy, i.e., if the temperature difference across the Peltier device is equal to zero, there is only a single entropy current, namely, the one given in Equ.(4.60). In general, however, the current of entropy is the sum of thermoelectric and conductive currents:

$$I_S = \alpha I_Q - G_S\left(T_2 - T_1\right) \tag{4.62}$$

G_S is the entropy conductance of the device. The thermoelectric voltage in Equ.(4.59), on the other hand, is the only electric potential difference between the electric capacitors if there is no flow of charge in the electric circuit. This is the case for open circuit conditions. Otherwise, the potential difference is the sum of thermoelectric and resistive parts:

$$U = \varepsilon\left(T_2 - T_1\right) + R_i I_Q \tag{4.63}$$

(This equation is analogous to what we have in the case of a battery having an internal resistance R_i. Note that a voltage is a negative electric potential difference.) The last two equations are the integral forms of the usual partial differential equation representation of thermoelectric processes (see Chapter 16).

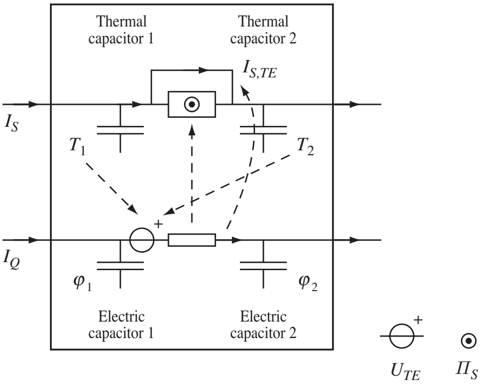

Figure 4.53: A dynamical model of a thermoelectric device. There are two storage elements for entropy (defining the temperatures of the cold and the hot end, respectively), and two capacitors (they define the high and low electric potentials). The elements comprise an electric generator ("electromotive force"), a coupled flow of charge and entropy, and conductive entropy and charge currents.

Naturally, we have to add relations for the irreversible effects of conductive transports of entropy and of charge as well as laws of balance of entropy and charge for the capacitors in the model of Fig. 4.53. The former lead to

$$\Pi_S = \frac{1}{T_2}\left(G_S\left(T_2 - T_1\right)^2 + R_i I_Q^2\right) \tag{4.64}$$

whereas the latter are best visualized in a complete system dynamics model diagram of a thermoelectric device. Fig. 4.54 provides an overview of the approach to thermoelectricity discussed here. Note the analogy between the structure of reservoirs and flows in the SD diagram and the capacitors and flows symbolized in Fig. 4.53.

Application of the dynamical model. The model presented in Fig. 4.54 is for a Peltier device such as the one pumping entropy from one body of water to another (see Fig. 4.8). To make use of the model it has to be completed by the dynamics of the bodies of water, entropy transfer to and from the device, entropy transfer to and from the environment, and data concerning the electric power supply used for driving the Peltier heat pump. Entropy transfer from water to the device is modeled according to what we have discussed above in Section 4.6.3 (see Fig. 4.49). There is also an entropy transfer "bypass" from the hotter to the colder fluid between the Peltier device and a lid on the double chambers of the container in Fig. 4.8. The parameters determining the thermal behavior of the tank in its environment can be obtained by an experiment that investigates the passive phenomena (thermoelectric device turned off) if we simply fill hot and cold water into the chambers and close the tank with a lid.

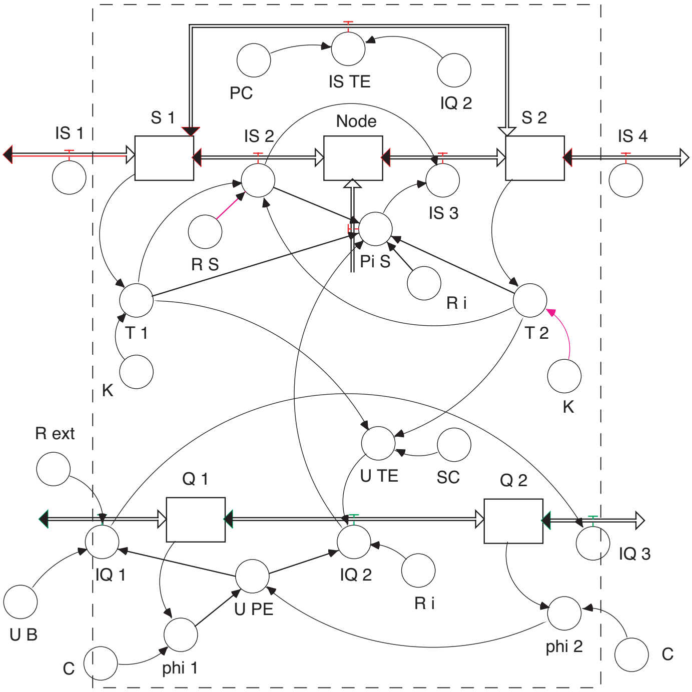

Figure 4.54: Diagram of a system dynamics model of a thermoelectric device. The structure of the model is depicted in Fig. 4.53. Note the representations of the four storage elements, two for entropy (hot and cold sides of the device) and two for electric charge (high and low electric potentials). There is a node taking the entropy production (Fig. 4.49) resulting from the conduction of entropy and charge. PC: Peltier coefficient, SC: Seebeck coefficient. R_S: entropy flow resistance; R_i: electric internal resistance. U_PE: terminal voltage of the device; U_TE: thermoelectric emf (Equ.(4.59)). IS_TE: nondissipative entropy current coupled to electric current (Equ.(4.60)). R_ext: Resistance of external electric circuit. U_B: voltage of external power supply (in pumping mode).

It does not make much sense to present data and simulation[28] together since agreement between the two is so close that the difference cannot be seen very well in a graph such as the one showing cooling of a body of water in Fig. 4.8.

Energy in thermoelectric processes. So far we have been able to analyze a thermoelectric device without recourse to energy considerations. We can hope to gain additional insight by appealing to the energy principle. Indeed, we will be able to derive the statement of the equality of the thermoelectric coupling coefficients (Seebeck and Peltier coefficients, see Equ.(4.61); this is called a reciprocity relation).

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[28] There is an important numerical problem to consider when one attempts to perform a simulation of the model in Fig. 4.54. Realistic estimates of entropy and charge capacitances yield values that are many orders of magnitude apart (the electric capacitances are exceedingly small). This leads to stiff differential equations that can be solved successfully (and accurately) with dedicated numerical methods but not with standard explicit codes.

To be specific, consider a Peltier device in generator mode (Fig. 4.55). It is operated between temperatures T_1 and T_2. Entropy production due to transfer to and from the device is assumed to be external to the system being analyzed, and the production of entropy due to electric conduction has been drawn separately to clarify the role of U_{TE} as the direct result of the thermoelectric effect. Entropy flows through the device as a consequence of the driving temperature difference. Now we must distinguish between two components of this entropy flux: the conductive current $I_{S,c}$ and the thermoelectric current $I_{S,TE}$; the latter is coupled to the current of electric charge according to Equ.(4.60). The conductive current is purely dissipative, the energy released due to its fall from T_1 to T_2 is used to produce entropy. This is different for $I_{S,TE}$, its fall is non-dissipative, the energy released is used to drive the electric current through the potential difference U_{TE}.

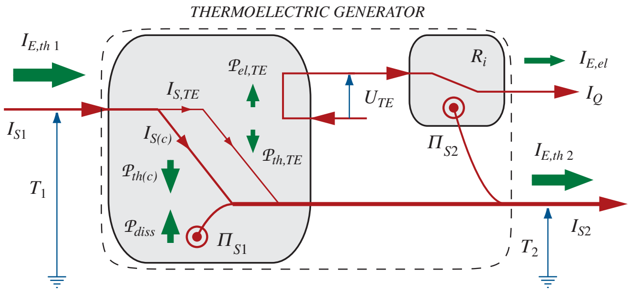

Figure 4.55: Process diagram of a thermoelectric generator. The electric (internal) resistor has been drawn separately to make the role of U_{TE} clear (note that $I_{E,el} < \mathcal{P}_{el,TE}$). $\mathcal{P}_{th(c)}$ is the power of the conductive current of entropy, $\mathcal{P}_{th,TE}$ is associated with the entropy current that is coupled to the flux of charge.

Equality of Peltier and Seebeck coefficients. This concludes the conceptualization of the role of energy in a thermoelectric process. We can now turn to a simple proof that the thermoelectric coupling coefficients α and ε should be equal. The thermal and electric thermoelectric powers are expressed by

$$\begin{aligned} \mathcal{P}_{th,TE} &= (T_1 - T_2) I_{S,TE} \\ \mathcal{P}_{el,TE} &= U_{TE} I_Q \end{aligned}$$

Since these expressions are equal, and since Equ.(4.59) and Equ.(4.60) hold for U_{TE} and $I_{S,TE}$, respectively, we have

$$\begin{aligned} (T_1 - T_2) I_{S,TE} &= U_{TE} I_Q \\ (T_1 - T_2) \alpha I_Q &= \varepsilon (T_1 - T_2) I_Q \end{aligned}$$

which proves the assertion that the Peltier and Seebeck coefficients must be equal.[29]

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[29] This is an example of what is called Onsager's reciprocity relations for "phenomenological" coefficients in coupled transports (such as thermo-diffusion and thermoelectricity). It is commonly assumed that the Onsager relations have to be proved by microscopic argument; see Jou et al. (1996), Woods (1975, Chapter 7). Thomson's (Lord Kelvin's) original argument (1882) bears some similarity to the one given above. The reason why the derivation is so simple here is the straightforward identification of the roles of $\mathcal{P}_{th,TE}$ and $\mathcal{P}_{el,TE}$. which parallels the distinction between entropy producing and non-dissipative processes in thermoelectric systems.

Second law efficiencies of thermoelectric devices. In Section 4.4.3, the Second Law efficiency was introduced as a natural measure of how well a device performs. For a simple engine such as in Fig. 4.35, it is equal to the power of the useful process divided by the power of the fall of entropy that drives the engine. This idea can be transferred to the case of thermoelectric generators (Fig. 4.55) and coolers (Fig. 4.56).

For a generator, the definition is straight forward. The second law efficiency equals the useful electric power (thermoelectric power minus power of electric resistive process) divided by the power of the fall of the entropy current I_{S1} from T_1 to T_2:

$$\eta_{\mathrm{II}} = \frac{\mathcal{P}_{el,TE} - R_i I_Q^2}{(T_1 - T_2) I_{S1}} = \frac{\varepsilon^2 R_L / (R_L + R_i)}{(R_L + R_i) G_S + \varepsilon^2} \tag{4.65}$$

This is the result for an ohmic load connected to the output of the thermoelectric generator. R_L is the electric resistance of the load (resistor), and R_i, G_S, and ε are the three parameters of the device (internal electric resistance, entropy conductance, and Seebeck coefficient, respectively). This result allows us to discuss how we might improve the efficiency under certain circumstances. For a given generator, we would want to find the load that optimizes the second law efficiency. Or given a certain type of application (load) we want to design the generator characteristics in order to improve the system performance.

The case of a thermoelectric cooler is similar. The Second Law efficiency can be defined as the ratio of the (useful) power of pumping the entropy current I_{S1} from T_1 to T_2 and the driving electric power $U_{ext} I_Q$ (see Fig. 4.56):

$$\eta_{\mathrm{II}} = \frac{(T_2 - T_1) I_{S1}}{U_{ext} I_Q} \tag{4.66}$$

After inserting the constitutive relations, we obtain an expression for η_{II} for given I_Q:

$$\eta_{\mathrm{II}} = \frac{\varepsilon I_Q - G_S (T_2 - T_1)}{\varepsilon (T_2 - T_1) I_Q + R_i I_Q^2} (T_2 - T_1) \tag{4.67}$$

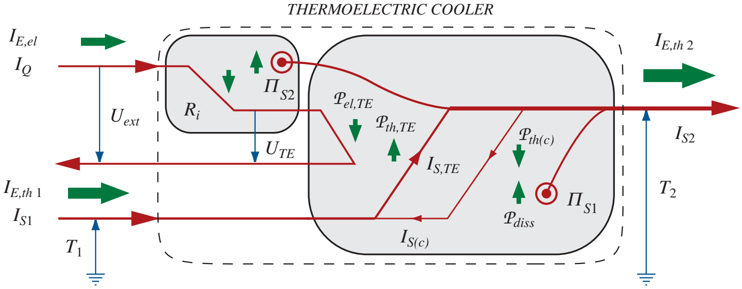


Figure 4.56: Process diagram of a Peltier heat pump. The electric (internal) resistor has been drawn separately to make the role of U_{TE} clear (note that $U_{ext} > U_{TE}$). $\mathcal{P}_{th(c)}$ is the power of the conductive current of entropy, $\mathcal{P}_{th,TE}$ is associated with the entropy current that is coupled to the flux of charge.

It is important to note that these equations denote the Second Law efficiencies calculated for the thermoelectric generator and cooler not taking into account entropy transfer to and from the devices (such as in Fig. 4.51). If we include the latter, the results will be considerably lower.

4.7.3 Structure of Thermocouples and Peltier Coolers

The foregoing discussion of the function of thermoelectric devices suggests that basically any single conductor should exhibit the features listed in Section 4.7.2. A wire made of copper going from a hot to a cold body transports entropy and charge, and the transports are (partly) coupled. However, it is clear that we cannot build an operating device in this manner. To let electricity flow, we need a closed circuit, so there needs to be a second conductor leading back from cold to hot (Fig. 4.57, left). If the second conductor is made of the same material it reverses the effect of the first; the same temperature difference will produce the reversed voltage making the device—called a *thermocouple*—electrically ineffective.

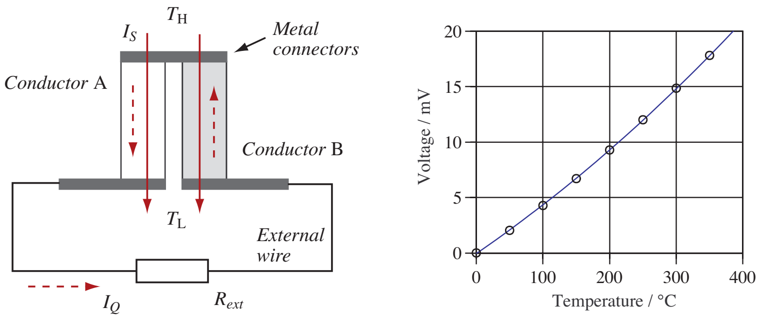


Figure 4.57: Left: A thermocouple is made of conductors of two different materials. Between two bodies at different temperatures T_H and T_L, it functions as a generator or a thermometer. (Entropy source and sink have to be insulated electrically from the thermocouple.) Right: Open-circuit voltage versus temperature difference for a T-type thermocouple made of copper and constantan (note that the relation is not perfectly linear).

Clearly, we must use a different material having a different Seebeck coefficient do have an effect. In Fig. 4.57, if $\varepsilon_A > \varepsilon_B$, electric charge can be conducted counter-clockwise. (Values of Seebeck coefficients for some metals and semiconductors are given in Table 4.8.)

Table 4.8: Seebeck coefficients at 0°C (relative to Platinum)[a]

Metals	Seebeck coefficient ε / µV/K	Semiconductors	Seebeck coefficient ε / µV/K
Aluminum	3.5	Ge	300
Bismuth	– 72	Se	900
Constantan	– 35	Si	440
Copper	6.5	Te	500
Gold	6.5	PbTe	– 180
Nichrome	25	Bi_2Te_3 (n-type)	– 230
Nickel	– 15	Sb_2Te_3 (p-type)	185
Platinum	0		
Silver	6.5		
Tungsten	7.5		

[a] The absolute Seebeck coefficient of Platinum is roughly 5 µV/K.

The discussion shows that the effective Seebeck coefficient of a thermocouple is the difference between the coefficients of the two materials employed. This is called the *differential Seebeck coefficient* (this is the coefficient ε in Equ.(4.59)). If we used just one conductor, say gold, and copper wires on a voltmeter, we could not even measure anything since copper and gold have effectively the same thermoelectric properties (see Table 4.8).

The effect becomes more pronounced if materials having positive and negative Seebeck coefficients can be used. This is the case for copper and constantan, to give just one example. The differential Seebeck coefficient of this combination is slightly more than 40 μV/K. A thermocouple made in this manner can be used as a thermometer.

Combining two strongly differing materials becomes essential if one wants to build thermoelectric coolers—otherwise the effect is just too small. Modern Peltier coolers are built with semiconductors where one leg of a thermocouple is a p-type and the other is an n-type conductor. If several or even many couples can be combined in series electrically and in parallel thermally, one obtains effective solutions for thermoelectric coolers (Fig. 4.58).

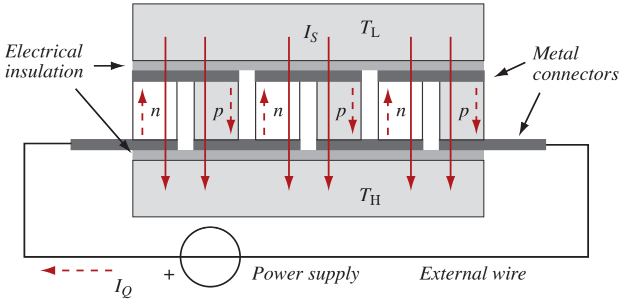


Figure 4.58: A combination of thermocouples made of n-type and p-type semiconductors can serve as an effective Peltier heat pump. Solid arrows: flow of entropy; dashed arrows: flow of electric charge. Note that the conductive flow of entropy which would be from the hotter to the colder body is not shown.

Take a closer look at a single thermocouple in Fig. 4.58. As charge flows through both legs of the couple to form a circuit, it flows up in one and down in the other. Since the first is an n-type material with negative Seebeck coefficient, entropy is pumped opposite to the flux of charge—here, this is downward from the colder to the hotter body. In the p-leg, entropy is carried in the same direction as charge flows. So both in the n-type and p-type semiconductors, entropy is pumped in the same direction.

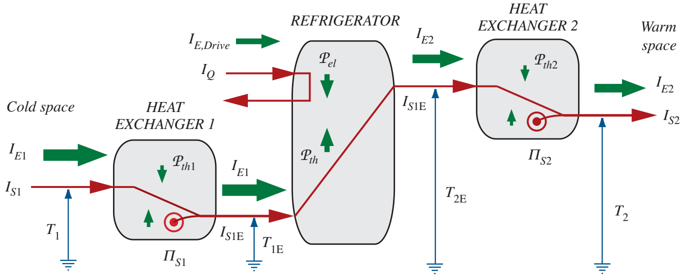
QUESTIONS

58. If we have a furnace at T_1 and a cooler at T_2, why can a heat engine not make use of the maximum temperature difference $T_1 - T_2$?
59. What does it mean to have an endoreversible engine? What is reversible in this case? How realistic is this model?
60. What does it mean to model the working fluid of a heat pump as a Carnot engine?
61. What is the main assumption concerning thermoelectric devices leading to the proof of equality of Seebeck and Peltier coefficients?
62. Why would a Peltier cooler with low entropy conductance be better than one with high conductance?

EXAMPLE 4.22. Cooling water in a refrigerator.

Five liters of water having a temperature of 25°C are placed in a refrigerator. They should be cooled at a constant rate to 8°C in 2 hours. Construct the following model. The working fluid of the refrigerator takes the entropy of the water from the cold space which is at 4°C. The fluid itself is then at a temperature of – 10°C. It emits entropy to the kitchen which has a temperature of 25°C. Assume the heat exchangers at the cold and the hot ends to have essentially equal dimensions. The thermal engine is supposed to operate endoreversibly. (a) Draw a process diagram of the system. (b) What is the entropy current emitted by the water at the beginning and toward the end of the process? (c) What is the entropy current entering the cold space and the working fluid? (d) What must the upper temperature of the working fluid be during rejection of the entropy taken up? (e) What must be the power driving the refrigerator? What is the *cop*? How does it compare to the *cop* of a completely reversible process?

SOLUTION: (a) The idea for the process diagram can be taken from Fig. 4.51. Here, entropy is pumped by the refrigerator. As always, entropy flows downward in the heat exchangers.



(b) The dynamics of the water is modeled according to Section 4.5 which yields

$$dS_w/dt = I_{S,w} \quad , \quad dS_w/dt = m\kappa\, dT_w/dt$$

$$I_{S,w} = m\kappa\, dT_w/dt = m\frac{c}{T}dT_w/dt = 5.0\frac{4200}{(25+273)}\frac{8-25}{7200}\frac{\text{W}}{\text{K}} = -0.166\frac{\text{W}}{\text{K}}$$

at $t = 0$ s. Toward the end, the temperature of water emitting entropy has changed to 8°C which gives a value of – 0.177 W/K for the entropy current.

(c) This current of entropy flows into the cold space and then through the heat exchanger at the cold end. Because of entropy production, the current entering the cold space will initially be

$$|I_{S1}| = |I_{S,w}| + \Pi_S = |I_{S,w}| + |I_{S,w}|\frac{T_w - T_1}{T_1} = 0.166\frac{\text{W}}{\text{K}} + 0.166\frac{25-4}{4+273}\frac{\text{W}}{\text{K}} = 0.179\frac{\text{W}}{\text{K}}$$

This value remains constant throughout the process (the energy current leaving the water is constant and it arrives at a constant 4°C). The current entering the working fluid at – 10°C is calculated in the same manner; the value obtained is 0.188 W/K.

(d) The entropy current rejected by the refrigerator is equal to the value calculated in (c). This current has to go through a heat exchanger equal to the one built at the cold end. The temperature difference needed for transfer is slightly higher than at the cold end:

$$T_{2E} - T_2 = (T_1 - T_{1E})\frac{|I_{S1E}|}{|I_{S1}|} = (4-(-10))\cdot\frac{0.188}{0.179} = 14.7\text{K}$$

So the temperature at the high end needs to be T_{2E} = 25°C + 14.7°C = 39.7°C.

(e) The entropy current $I_{S1\mathrm{E}}$ must be pumped from $T_{1\mathrm{E}}$ to $T_{2\mathrm{E}}$. The power of this process is

$$\mathcal{P}_{th} = \left(T_{2E} - T_{1E}\right) I_{S1E} = \left(39.7 - (-10)\right) \cdot 0.188\,\mathrm{W} = 9.34\,\mathrm{W}$$

The definition of the *cop* of a refrigerator differs slightly from that of a heat pump given in Equ.(4.29). Here it is

$$cop = \frac{I_{E1}}{\mathcal{P}_{drive}} = \frac{T_{1E} I_{S1E}}{\mathcal{P}_{th}} = \frac{263 \cdot 0.188}{9.34} = 5.3$$

The *cop* of a completely reversible refrigeration process between T_L and T_H is

$$cop = \frac{T_\mathrm{L}}{T_\mathrm{H} - T_\mathrm{L}}$$

If entropy leaves the water to be cooled at 25°C and enters the kitchen at 25°C, the *cop* should theoretically be infinitely high. Toward the end with the water at 8°C the cop becomes 16.5.

EXAMPLE 4.23. Cooling water with a thermoelectric cooler.

DATA

Device data from manufacturer:

$R_i = 0.98\ \Omega$
$\varepsilon = 0.050$ V/K
Size: 6.0 cm by 6.0 cm

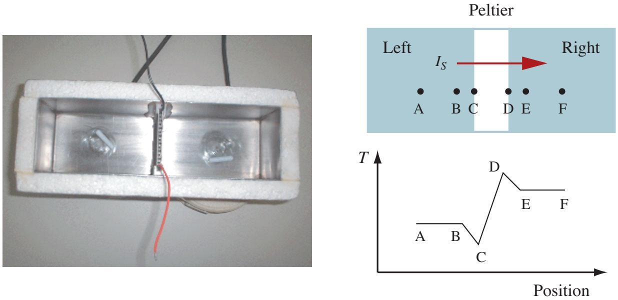
Experimental results at $t = 1000$ s:

$m_w = 0.54$ kg
$G_{S,leak} = 2.0 \cdot 10^{-3}$ W/K^2
$U_{ext} = 1.41$ V
$I_Q = 1.04$ A
$T_{w1} = 296.7$ K
$T_{w2} = 300.7$ K
$dT_{w1}/dt = -1.10 \cdot 10^{-3}$ K/s
$dT_{w2}/dt = 1.9 \cdot 10^{-3}$ K/s

In the experiment reported in Fig. 4.8, water in a sealed chamber is cooled with the help of a Peltier device (the water is stirred). The entropy is rejected to a second body of water in the same container. Manufacturer data and experimental data is given in the box on the side. (a) Sketch a qualitative temperature position diagram going from the first to the second body of water. (b) Determine the thermoelectric voltage of the device and use this to find the temperature difference from one side to the other of the cooler. (c) Determine the entropy current leaving the first body of water at $t = 1000$ s. Note that there is a leak around the Peltier device going from the warmer body of water to the colder one; the leak can be quantified by an entropy conductance of $2.0 \cdot 10^{-3}$ W/K^2. (d) What is the entropy current through the Peltier device coupled to the electric current? Use this to find the conductive entropy current through the cooler and the entropy conductance of the device. (e) Estimate the entropy and energy transfer coefficient from water to the Peltier device. (f) Calculate the energy current emitted by the cooling water and determine the *cop* of the process.

SOLUTION: (a) The temperature of the water is uniform. The temperature must drop from the cooling water to the surface of the Peltier device for entropy to flow out of the liquid. In the device, the temperature rises to a value above that of the body of water that accepts the entropy. So the temperature drops from the warm surface of the thermoelectric cooler to the second body of water.

Figure Ex.23



(b) In the experiment, both the total voltage across the Peltier device, U_{ext}, and the electric current I_Q were measured. Since the internal resistance R_i is specified by the manufacturer, we can calculate the voltage of the thermoelectric generator U_{TE} from simple circuit theory:

$$U_{TE} = U_{ext} - R_i I_Q = 1.41\,\mathrm{V} - 0.98 \cdot 1.04\,\mathrm{V} = 0.39\,\mathrm{V}$$

Once the thermoelectric voltage is known, the associated temperature difference across the device (from C to D in Fig. Ex.23.1) can be calculated:

$$U_{TE} = \varepsilon\left(T_2 - T_1\right) \quad \Rightarrow \quad T_2 - T_1 = U_{TE}/\varepsilon = 0.39/0.050\,\mathrm{K} = 7.8\,\mathrm{K}$$

(c) To obtain the entropy current pumped from the body of water being cooled, we start with the law of balance and the constitutive capacitive and resistive relations:

$$\begin{aligned} &dS_w/dt = I_{S,w} + I_{S,leak} \\ &dS_w/dt = m\kappa\, dT_w/dt \\ &I_{S,leak} = G_{S,leak}\left(T_{w2} - T_{w1}\right) \end{aligned}$$

The mass of the body of water, its temperature and rate of change of temperature at $t = 1000$ s have been obtained from the experiment. Together with the conductance of the entropy leak between the bodies of water we have:

$$\begin{aligned} &I_{S,w} = m\kappa\, dT_w/dt - I_{S,leak} = m\frac{c}{T} dT_w/dt - G_{S,leak}\left(T_{w2} - T_{w1}\right) \\ &= 0.54\frac{4200}{296.7}\left(-1.1 \cdot 10^{-3}\right)\frac{\mathrm{W}}{\mathrm{K}} - 2.0 \cdot 10^{-3}\left(300.7 - 296.7\right) = -16.4 \cdot 10^{-3}\,\frac{\mathrm{W}}{\mathrm{K}} \end{aligned}$$

(d) The Peltier cooler pumps an entropy current equal to

$$I_{S,TE} = \varepsilon I_Q = 0.050 \cdot 1.04\,\mathrm{W/K} = 5.2 \cdot 10^{-2}\,\mathrm{W/K}$$

from C to D in Fig. Ex.23. Since the current leaving the water at point B is only 16.4 mW/K, there must be a conductive flow of entropy through the cooler (from D to C) as a result of the temperature difference $T_D - T_C$. If we assume the entropy production due to transfer from the water to the cooler to be negligibly small, we have

$$\begin{aligned} &\left|I_{S,w}\right| = \left|I_{S,TE}\right| - \left|I_{S(c)}\right| \quad \Rightarrow \\ &\left|I_{S(c)}\right| = \left|I_{S,TE}\right| - \left|I_{S,w}\right| = 5.2 \cdot 10^{-2}\,\mathrm{W/K} - 16.4 \cdot 10^{-3}\,\mathrm{W/K} = 3.56 \cdot 10^{-2}\,\mathrm{W/K} \end{aligned}$$

This allows us to find the conductance of the cooler:

$$I_{S(c)} = G_S\left(T_2 - T_1\right) \quad \Rightarrow \quad G_S = \frac{I_{S(c)}}{\left(T_2 - T_1\right)} = \frac{3.56 \cdot 10^{-2}}{7.8}\frac{\mathrm{W}}{\mathrm{K}^2} = 4.56 \cdot 10^{-3}\,\frac{\mathrm{W}}{\mathrm{K}^2}$$

(e) The temperature drops from the first body of water to the cooler, and from the cooler to the water at higher temperature. From B to C and from D to E we have two convective transfer layers. It is reasonable to assume that the temperature differences across the layers are the same at the cool and the warm ends. Since we have 7.8 K from C to D, and 4.0 K from B to E, there is a temperature drop of 1.9 K for each of the convective layers:

$$\begin{aligned} &I_{S,w} = G_{S,wP}\left(T_1 - T_{w1}\right) = A\, h_{S,wP}\left(T_1 - T_{w1}\right) \quad \Rightarrow \\ &h_{S,wP} = \frac{I_{S,w}}{A\left(T_1 - T_{w1}\right)} \approx \frac{16.4 \cdot 10^{-3}}{0.060^2 1.9}\frac{\mathrm{W}}{\mathrm{K}^2\mathrm{m}^2} = 2.4\,\frac{\mathrm{W}}{\mathrm{K}^2\mathrm{m}^2} \end{aligned}$$

The entropy transfer coefficient can easily be converted to the equivalent energy transfer coefficient:

$$h_{wP} \approx T_{w1} h_{S,wP} = 297 \cdot 2.4 \frac{\mathrm{W}}{\mathrm{K} \cdot \mathrm{m}^2} = 710 \frac{\mathrm{W}}{\mathrm{K} \cdot \mathrm{m}^2}$$

(f) The energy current from the body of water to the Peltier device is obtained from the entropy current and the associated temperature:

$$I_{E,w} = T_{w1} I_{S,w} = 296.7 \cdot \left(-16.4 \cdot 10^{-3}\right) \mathrm{W} = -4.87 \mathrm{W}$$

The *cop* is defined as the magnitude of this current divided by the power of the electric process driving the pump:

$$cop = \frac{\left|I_{E,w}\right|}{U_{ext} I_Q} = \frac{4.87}{1.41 \cdot 1.04} = 3.3$$

This compares to a *cop* of 74 for a completely reversible process of pumping entropy from the cool to the warm water.

4.8 ENTROPY PRODUCTION, SYSTEMS, AND WALLS

Now that we have seen how a theory of the dynamics of heat can be constructed and applied in simple settings, let me return to some general considerations concerning thermal systems and how to analyze them.

In any physical analysis, there is always an important element to be considered. The analyst has to be clear about which system or body is being studied. Only then can the application of a law such as the law of balance of entropy work out successfully. In many situations, it is quite clear which system has been chosen for investigation, and we do not have to be particularly explicit about our choice. However, nowhere is it more important to be precise and explicit about which part of the world we are going to study than in thermodynamics. The very nature of heat — its tendency to increase through production — calls for careful analysis. We cannot be vague about where the production of entropy occurs in a given situation. Careless treatment of this problem has caused many confusing statements about thermal processes.

The first point to be kept in mind is that analysis of a situation applies only to the system chosen and to nothing else. Specifically, this means that the production of entropy takes place *inside the system*. No matter what might happen in the surroundings of the system, dissipation is related to that particular system only. If a body undergoes reversible changes while entropy is being created outside of it, we have to conclude that as far as our equations are concerned, entropy has not been produced. Our analysis cannot make a statement about anything but the body being studied. Conversely, if a process is irreversible, dissipation must have occurred in the body or we would not know about it.

This raises a second point. Consider a body at a uniform temperature in an environment of uniform, but different, hotness. Body and environment touch at the surface of the body. The surface is shared by both the system and its surroundings so you might ask, what is the temperature of the surface? Is it the temperature of the body, or of the environment? The problem becomes more acute if we consider the balance of entropy for a current across this surface. The geometrical surface certainly does nothing to disturb the flux of energy accompanying the current of entropy. In other words, the current of energy must be continuous across the surface (Fig. 4.59). Therefore the current of entropy must be discontinuous; it increases in the direction of flow from the hotter to the cooler body. But then, where has entropy been produced? Where is the seat of dissipation? Unless we are prepared to treat the boundary between body and environment as a physical system in its own right, there is no system which can account for the production. Dissipation must take place in a proper physical system. Therefore, we are led to introduce surfaces or *ideal walls* across which temperature, entropy flux, and flux of energy are continuous. Such walls do not add to the processes occurring inside a system, particularly to the production of entropy.

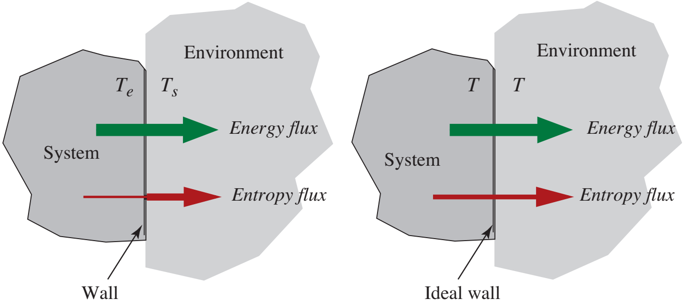


Figure 4.59: If we allow for the system and its environment to be separated by a wall across which the temperature is discontinuous, a current of entropy crossing this boundary will have to be discontinuous as well. Since this brings up the problem of where entropy has been produced, we conceive of ideal walls which do not add to dissipation. Temperature, entropy flux, and flux of energy are all assumed to be continuous across such a wall.

The puzzle presented by two systems at different temperatures can be solved in a number of ways. The ideal system wall may be placed in such a way that the dissipation takes place inside the system. Alternatively, we may exclude the drop of temperature from the system, thereby putting the burden on the analysis of the environment as a physical system. Finally, we may introduce a third system, a finite three-dimensional wall separating the first system and its surroundings. This third body is made responsible for the production of entropy due to the flow of heat from the hotter to the cooler body. The finite wall cannot have a uniform temperature. It exists for communicating between the system and its environment in a physically acceptable way. It is a body with all the physical attributes of the systems we are studying in this book. Like every proper system it, too, is assumed to be surrounded by an ideal wall.

In essence, then, we consider physical systems having ideal walls. Transfer of entropy and energy across such a wall into or out of the body is governed by the basic relationship between entropy flux, temperature, and associated energy current, Equ.(4.21):

> *At the surface of a system, the current of entropy and the flux of energy associated with it are related by the temperature at the surface according to Equ.(4.21). Possible production of entropy may take place inside the system, but not at its ideal wall.*

The assumptions stated here are fundamental for thermodynamic analysis. They facilitate the understanding of where and how dissipation may occur. In particular, they do away with statements about thermal energy being added to bodies reversibly or irreversibly. There is no such thing as an irreversible exchange of entropy and energy. The exchange takes place across an ideal wall and is always governed by Equ.(4.21), and by nothing else. If any entropy has been produced, it will have taken place inside the system being analyzed.

By the way, if ideal walls did not exist, it would be hard to imagine how temperatures could be measured. A thermometer is a physical system. If its surface were not ideal it might show a different temperature from that of the immediate neighborhood. This point will be of great importance when we create a formal theory of the dynamics of heat in Chapters 10-12.

EXERCISES AND PROBLEMS

1. In what sense is hotness the intensity of heat? Why do we have to distinguish it from quantities of heat? What other quantities in physics may the intensity of heat be compared to?
2. Consider a moving body that splits into two halves which continue moving along together. Which mechanical quantity is divided among the bodies? Which other mechanical variable is not divided up, leaving each of the parts with its initial value? Compare electrical and thermal phenomena to this mechanical example. Which electrical or thermal quantities correspond to the mechanical variables?
3. List everyday phenomena which are responsible for our intuitive notion of heat content of bodies. Can you turn the qualitative idea into a physical quantity having a precise meaning?
4. Why shouldn't we think of energy as a mechanical, electrical or thermal quantity? Why would it be particularly wrong to identify stored energy as mechanical, electrical, thermal or other? What consequence does this have for identifying "heat" as stored energy?
5. What happens to all bodies under all circumstances if their energy is increased? Which physical quantity changes if this happens? What kind of conclusions *cannot* be drawn from the statement that the energy of a body has changed?
6. With the help of physical quantities, explain the *difference* between making a body rotate and making it warmer.
7. Compare different fluidlike physical quantities such as momentum, charge, amount of substance, and entropy. Which two properties do they all have in common? What are possible differences between the quantities listed?
8. Rephrase the following expressions in terms of entropy. In which cases would reference to energy be clearly wrong? Do any of the terms and expressions have nothing to do with entropy? (a) heat engine, heat pump; (b) heat exchanger; (c) heating and cooling; (d) heat flow, transfer of heat; (e) convective heat flow; (f) heat source; (g) storage of heat, heat reservoir; (h) phenomena in which heat causes motion; (i) solar heater; (j) production of heat; (k) heat transfer coefficient; (l) pumping heat from the cold enclosure; (m) heating power.
9. A copper bar having a constant cross section and length l_o is rigidly attached between walls. Assume it to be free of stress at a given temperature. If the temperature changes, the length of the bar changes, and momentum currents due to compression or tension are set up in the bar. Calculate the thermal stress resulting from a change of temperature of ± 30°C. Young's modulus for copper is equal to $12.3 \cdot 10^{10}$ N/m^2.
10. Assume that a solid cube expands by expanding along each of its three axes equally. Show that the coefficient of volume expansion equals $3\alpha_l$ in this case, where α_l is the (linear) coefficient of expansion. What is the relative change of volume per degree Celsius of a cube of 1 kg copper?
11. It is found that the current through the tungsten filament of a light bulb is 0.010 A at a voltage of 1.0 V. At 150 V the current is equal to 0.50 A. What is the temperature of the filament at the higher reading, if the experiment is performed at room temperature (20°C)? The temperature coefficients are $\alpha = 4.11 \cdot 10^{-3}$ K^{-1} and $\beta = 9.62 \cdot 10^{-7}$ K^{-2} for the tungsten filament.

12. Measurements demonstrate that dilute gases show a linear relationship between volume and temperature, if the pressure is kept constant. (a) Express the law in a form equivalent to that of Equ.(4.8). Compare it with the linear approximation to the law of expansion of liquids and solid s and calculate the coefficient of expansion with respect to a temperature of 0°C. Is the coefficient independent of temperature? (b) It is found by measurement that $\alpha^*(0°\text{C}) = 1/273.15$ K. Show that the ratio of the volumes at different temperatures (for equal pressure) is given by the ratio of the Kelvin temperatures.

13. Formulate the law(s) of balance of entropy in instantaneous (dynamical) and integrated forms for the following situations. (a) A uniform material is heated but not cooled. (b) Water in an open container is heated electrically and stirred at the same time. (c) A liquid in a well insulated container is stirred mechanically. (d) A viscous gas is compressed in a well insulated cylinder. (e) A hot stone cools in cold water inside a well insulated container. Take the stone and water first as separate systems, then as a single system. (f) Hot water cools in a thick walled container in a cool environment (take water and container as separate systems). (g) Water is heated in a tea kettle but it is not getting any hotter.

14. A body is heated and cooled at the same time. At one end, entropy flows into the body at a rate of 300 W/K. At the other end, entropy is removed at a rate of 200 W/K. What is the net heating, or the net entropy flux for the body? At what rate does the entropy content of the body change? Assume that entropy is conserved in this process.

15. A constant flux of entropy of 200 W/K leaves a system, while a current entering the system changes according to $-20 \text{ W/(K}\cdot\text{s)}\cdot t$. (a) How much entropy is absorbed and emitted in the first 15 s? Refer the absorbed entropy to the current flowing into the system, and the emitted entropy to the current flowing out of the body. (b) How much entropy is exchanged in total? (c) What is the change of the entropy content of the body?

16. A body which is being heated undergoes an irreversible process. The net current of entropy changes from – 100 W/K to zero in 20 seconds. During this time, the rate of creation of entropy is equal to 30 W/K. (a) What is the rate of change of the entropy in the body? (b) How large are the exchanged entropy and the change of entropy content in the first 20 s?

17. Give a graphical interpretation of the energy exchanged in thermal processes during the ideal Carnot cycle and represent the thermal work in the *TS* diagram.

18. (a) Consider a Carnot cycle, i.e. a cycle where entropy is absorbed and emitted at constant temperatures, for which the adiabatic expansion is dissipative. Draw the *TS* diagram and indicate the energy exchanged in the thermal processes. (b) Why is the cycle less efficient than its reversible counterpart? (c) Identify the lost available energy in the *TS* diagram.

19. An immersion heater has a temperature of 120°C as it emits an energy current equal to 0.80 kW. (a) How large is the current of entropy flowing across the surface of the heater? (b) If the temperature of the water receiving the heat is equal to 80°C, how much entropy flows into the water?

20. Consider water being heated by an immersion heater. (a) If you consider the body of water as a system, what is its equation of balance of entropy? (Assume the distribution of entropy through the system to take place reversibly; what does this mean for the conduction of entropy through the system?) (b) Answer the question for the case in which you take the system to be made up of water plus heating coil.

21. A metal bar conducts entropy from a container of boiling water to a mixture of ice and water. It is found that in the latter container, ice melts at a rate of 10.0 g per minute (see Table 4.3). Compute the rate at which entropy is produced in the conductor.

22. A small steel sphere falls in oil. The frictional force is calculated according to Stokes' law. What is the maximum rate of creation of entropy if the temperature of the medium is 20°C? Take the radius of the sphere to be 1 mm. The densities of steel and oil are 7700 kg/m^3 and 960 kg/m^3, respectively. The dynamic viscosity of oil is 0.99 Pa·s.

23. A large thermal power plant (such as a nuclear power plant) takes its entropy from a reactor at 600 K. The entropy is emitted again to the cooler at 300 K. The measured useful power

is 1.0 GW. (a) Sketch a process diagram (with carrier and energy currents) for the system (the system between reactor and cooler). (b) If the heat engine could operate ideally, what would be the entropy current through the engine? (c) The thermal efficiency of the power plant is only 30%. What must the real entropy current and energy current from the reactor to the heat engine be? (d) What is the entropy production rate in the heat engine (i.e., between the reactor and the cooler)? (e) What is the total entropy production rate (i.e., including the one in the reactor)?

24. A car engine is running at steady-state. Gasoline provides energy at a rate of 400 kW, the measured mechanical power of the engine is 100 kW. The entropy is provided at a temperature of 900 K and cooling takes place at 300 K. (a) Sketch a process diagram for the engine as a single system between "furnace" and "cooler." (b) What is the entropy current into the engine? (c) What is the thermal power? (d) What would the entropy current to the cooler be if the engine were operating ideally? What would the energy current to the cooler be? (e) What is the actual energy current to the cooler? (f) What is the entropy production rate in the engine?

25. A heat pump is used to heat water at 60°C. Heat is taken from the ground at 2°C. The observed coefficient of performance is 2.2 while the energy current associated with heating has a magnitude of 1.0 kW. (a) How large is the rate of production of entropy? (b) How large is the loss of available power? Show that it is equal to the product of the rate of generation of entropy and the temperature of the environment. (c) How large is the second law efficiency of the heat pump?

26. The temperature inside a freezer is kept at a constant – 23°C. The ambient temperature is 20°C. According to the technical information booklet, the freezer uses 1.2 kWh of electrical energy per day. We model the freezer as a coupled system (insulation, container, ideal heat pump, and heat exchangers). The heat pump pumps the heat reversibly from – 38°C to 42°C. (a) Calculate the entropy flow through the heat pump. (b) What is the energy current flowing into the freezer due to the temperature difference to the environment? (c) In our model, entropy is produced in three processes. Show where this happens in your sketch of the model. (d) What is the total rate of entropy production?

27. Determine the mechanical power of a thermomechanical engine undergoing a steady-state cyclic process. The engine works irreversibly. It is in contact with n heat reservoirs of constant temperatures, and with the environment at temperature T_o. Identify the loss as a result of dissipation, and compute the second law efficiency of the heat engine.

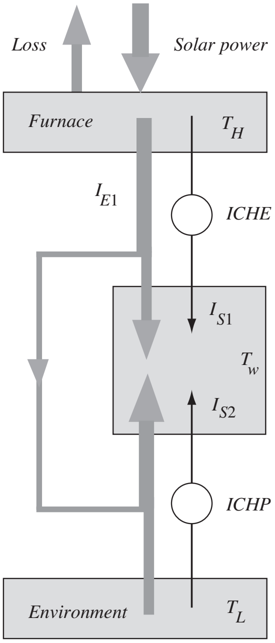


Figure P.28

28. Not all types of solar heating are created equal (Fig. P.28). Consider the following means of keeping a supply of domestic water at 60°C. In a first setup (A), solar radiation is used directly to heat the water. In a second (B), solar radiation is used to heat a furnace to 700°C. The entropy from the furnace drives an ideal Carnot engine (*ICHE*) which rejects the entropy to the water at 60°C. The energy released by the engine is used to drive an ideal Carnot heat pump (*ICHP*) which pumps entropy from the environment at 0°C into the water at 60°C. Calculate the ratio of the rates of heating of the two processes. Take I_{E1} to be equal in both cases.

29. We are given a certain amount of hydrogen which we are to use for heating water. The water is to be kept at a constant temperature T which is higher than that of the environment (T_a), and lower than a possible flame temperature if we decide to burn the hydrogen. (a) Calculate the heating power for the water in terms of the energy released by the chemical reaction of hydrogen with oxygen for the following three modes of heating: (A) direct heating by burning the hydrogen; (B) heating with the help of an ideal heat engine driven by entropy from a furnace at temperature T_f which receives its entropy from burning of hydrogen, and an ideal heat pump driven by the heat engine (scheme B of Problem 28); (C) heating with the help of an ideal heat pump driven by an ideal fuel cell which uses the hydrogen. (b) Calculate the loss of power for scheme A, and show that it is equal to the product of the temperature of the water and the rate of production of entropy.

30. Measurements put the value of the entropy capacitance of 1 kg of ice at 8.1 J/K^2 at a temperature of 13°C below freezing, and at 7.7 J/K^2 at a temperature of 0°C. (a) Calculate the

current of entropy which is needed if a lump of ice having a mass of 1kg at a temperature of –13°C is to be heated so that its temperature rises by 1 K per minute. (b) Estimate the total entropy transmitted to the body if it is to be heated up to a temperature of 0°C.

31. How much entropy and energy are added to 1.0 kg of silicon if the body is heated from 160 K to 640 K? (See Fig. 4.41 for properties of silicon.)
32. A body made of a material having (known) variable entropy capacitance is heated (the current of entropy is assumed to be prescribed). (a) Represent the process by a system dynamics model diagram. (b) Write all the equations and derive the differential equation for the temperature of the body.
33. A rigid body has a constant entropy capacitance in a particular range of temperatures. How much energy does it emit if its temperature drops from T_i to T_f?
34. An ideal Carnot engine is driven with the heat from 2000 liters of water at 90°C. Entropy is rejected to the environment at a temperature of 20°C. How much energy does the engine release for mechanical purposes?
35. In an experiment, glycol was heated electrically in a perfectly insulated container. Electric power and temperature of glycol were recorded as functions of time. The mass of the glycol was measured. The experiment was used to determine the temperature – specific entropy diagram (see Fig. P.35.1). (a) Explain how the *Ts* diagram can be determined from the data of the experiment. (b) Determine the specific entropy capacitance of glycol at 300 K, 340 K and 380 K. What is your observation? (c) Use the results to determine the specific heat (specific temperature coefficient of energy). Is this quantity constant or does it increase or decrease with temperature? (d) Glycol is heated electrically at constant power in a perfectly insulated container. What would the temperature as a function of time be (qualitatively)? Why? (e) Glycol having a mass of 0.50 kg is heated at constant electric power of 20 W inside a sealed aluminum can. The temperature of the environment is 295 K. Explain why we get the measurements (temperature as a function of time) as shown in the graph (Fig. P.35.2). (f) Use the data to determine the entropy conductance of the aluminum can.

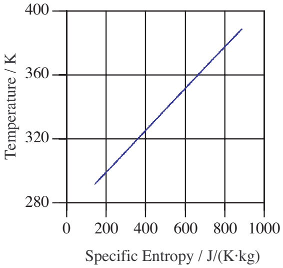


Figure P.35.1

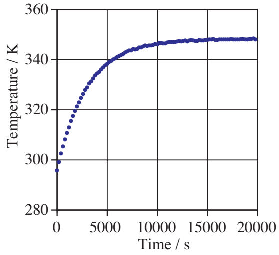


Figure P.35.2

36. Hot water is filled into a thin-walled polished aluminum can. The water is stirred continuously. Data: Radius of can: 3.3 cm; height of can: 15.0 cm; mass of water: 490 g. The inside heat transfer coefficient is very high, the metal sheet is very thin. Lid and bottom are insulated. Power of the mixer: 2.0 W; temperature of the ambient is a constant 19°C. The temperature of the water has been measured as a function of time (see Table 4.9). (a) Explain the experimental data. (b) Sketch a diagram of a system dynamics model of the system and processes. (c) Write down all the equations of the model. (d) Determine the convective entropy and heat transfer coefficients at the outside surface of the polished can, and the power of the magnetic bar used for mixing.

Table 4.9: Water temperature

t / s	*T* / °C	*t* / s	*T* / °C	*t* / s	*T* / °C
0	86.84	25000	30.74	50000	27.10
5000	58.44	30000	29.34	55000	27.05
10000	44.54	35000	28.45	60000	27.00
15000	37.30	40000	27.80	65000	26.95
20000	33.32	45000	27.40	70000	27.00

37. The inside and the outside of a house are at temperatures of 25°C and 35°C, respectively. If all doors and windows are closed, the home has an energy conductance of 300 W/K. There is no sunlight getting inside. (Imagine the house as an airtight and opaque box.) If we do not cool the house, the inside temperature will be 31.3°C after 10 hours. (a) Determine the entropy capacitance and the temperature coefficient of energy of the house. (b) What is the entropy current arriving inside at 25°C? (c) A heat pump is used to keep the

inside at 25°C. If the heat pump worked ideally, what would the power driving it be? (d) The coolant of the heat pump takes up entropy in the house at 10°C. It emits it at 45°C. What is the (minimal) real power for driving the pump?

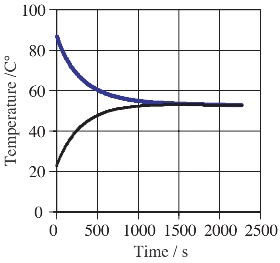


Figure P.38

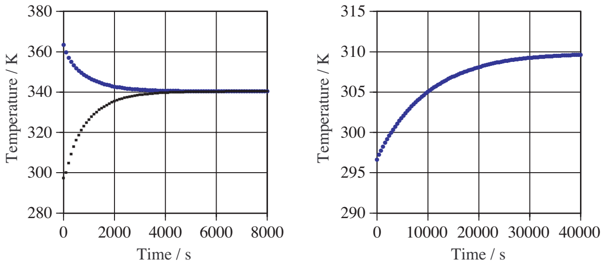
38. Two amounts of water having equal mass of 0.951 kg each are inside two chambers separated by a thin metal wall. The dimensions of the chambers are 10 x 10 x 10 cm. The container chambers are well insulated from the environment. Hot water is filled into one of the chambers, cold water into the other. The water is thoroughly mixed the whole time. The temperatures are measured as functions of time (Fig. P.38). (a) What is the convective heat transfer coefficient from the water to the metal wall? Note that the thermal resistance of the metal wall is itself very small. (Use the data of the experiment and neglect heat loss to the environment and the effect of the mixer). (b) What is the change of energy of each of the bodies of water during the first 500 s? (c) Use the data to determine as carefully as possible the entropy conductance (or the energy conductance) for heat loss to the environment for the entire container. The power of the mixers in the two chambers adds up to 1.0 W, and the ambient temperature is equal to 22°C.

39. Two different experiments are performed with a thick-walled PVC container. They are used to determine the specific heat (specific temperature coefficient of energy) and the thermal conductivity (energy conductivity) of PVC. When you have found these values, also determine the specific entropy capacitance and the entropy conductivity. Data for the container: Inside radius: 3.0 cm, outer radius: 4.65 cm, inside height: 0.105 m, density: 1400 kg/m^3.

    Experiment 1: The container is completely insulated from the environment. It has an initial temperature of 23.4°C and is filled with hot water having a temperature of 89.5°C. Everything is now sealed, and the water temperature and the temperature at the middle of the container wall are measured (see graph Fig. P.39, left).

    Experiment 2: Lid and bottom are perfectly insulated. Water and container have an initial temperature of 23.4°C, the same value as the (constant) temperature of the environment. The mixer dissipates energy at a rate of 2.0 W. Take values of 200 W/(K·m^2) and 13 W/(K·m^2) for the heat transfer coefficients on the inside and the outside of the PVC container. Fig. P.39, right, shows the water temperature as a function of time.

Figure P.39



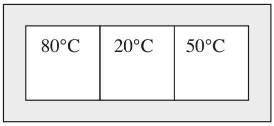


Figure P.40

40. A container consists of three chambers made of thin metal sheets. Each chamber has a a size of 10 by 10 by 10 cm. The chambers are touching as shown in the figure. Each of them is filled with one liter of water. The initial temperatures are 80°C, 20°C, and 50°C, respectively. The assembly is perfectly insulated from the environment. Neglect dissipation due to stirring. (a) What does “thermally insulated” mean in a formal model? Explain using words and equations. (b) Is there entropy production in this system if we neglect stirring? (c) Sketch the diagram of a system dynamics model that can be used to simulate the behavior of the system. Use the energy representation. (d) The convective heat transfer coefficient from water to metal is 400 W/(K·m^2). Determine the (energy) conductance from the water in one chamber to the water in the adjacent chamber. (e) Determine the rates of change of the three temperatures right at the start. (f) Sketch the temperatures as functions of time. Use calculations to make the sketch as realistic as possible (show time constants).

41. A person is taking a shower and changes the position *P* of the lever of the shower mixer to adjust the temperature of the water (water is mixed from cold (T_C) and hot (T_H) water). The mixing temperature is given by

$$T = T_C + \left(T_H - T_C\right)P$$

where *P* is a number between 0 and 1. Zero means that only cold water is used, one means that only hot water comes out of the shower. In the figure, you see a diagram of a possible model of how the position *P* is adjusted by the person to a desired water temperature (T_D).

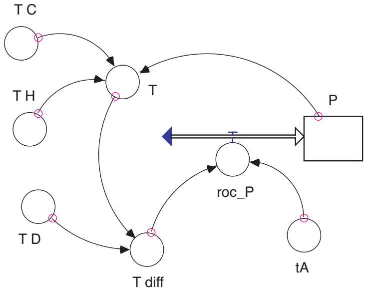


Figure P.41

(a) Derive the equation presented above for the mixing temperature of water. (b) The person changes the position *P* of the lever at a rate *roc_P* that depends linearly upon the difference of desired and actual temperatures. In the model, the process of adjustment introduces a kind of inertia t_A (larger inertia means slower adjustment). Formulate the equation for *roc_P* that corresponds to these ideas. (c) Formulate all the equations of the model. (d) Transform these equations into a single differential equation for the position *P* of the lever. (e) Assume 20°C and 60°C for cold and hot water, respectively, and 40°C for the desired temperature. Take a value of 50 K · s for the factor of inertia t_A. What is the time constant of this model? (f) Sketch the temperature of the water for the parameters according to problem (e) (show time constant and asymptote). Assume the initial condition to be $T(0) = 20$°C (Position $P(0) = 0$).

42. Two bodies of water of 0.50 kg each are separated by a Peltier device. The bodies are completely insulated from the environment. The Peltier device is driven electrically. It pumps entropy from the colder into the warmer water. The device works by creating a cold and a hot side. We consider a certain moment. Values of temperature, electric current and resistance are given in the table.

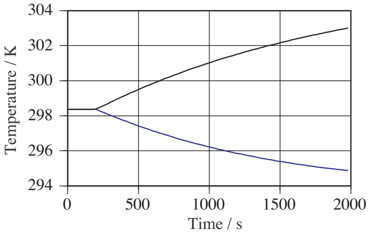
Table 4.10: Data for water and Peltier device

	Cold	Hot
Temperature of water	295.7 K	301.7 K
Temperature of Peltier device	294.5 K	303.4 K
Entropy current into/out of water	0.0122 W/K	0.0169 W/K
Electric current through device	1.02 A	
Electric resistance of device	0.98 Ω	

(a) Estimate the entropy production rate due to the electric process. (b) The entropy current leaving the cold water is 0.0122 W/K, the current into the warm water is 0.0169 W/K. What is the total entropy production rate in the system? What is the fraction due to electric dissipation? (c) If the entire process were completely reversible, how much energy would be needed per second to pump the entropy current of 0.0122 W/K from the cold into the warm water? (d) The voltage that powers the Peltier device is 1.5 V. What is the efficiency of the device?

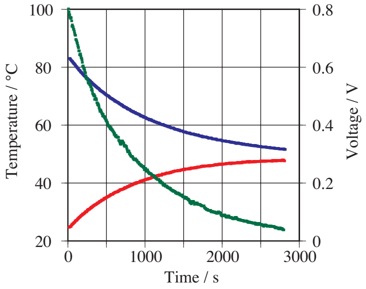
43. A Peltier device is used to separate two bodies of water in an otherwise perfectly insulated container (see Example 4.23). The Peltier device is operated as a heat pump. In the diagram, the temperatures of the two bodies of water are shown as functions of time. Data: Mass of a body of water: 0.50 kg; electric current through Peltier Device: 1.03 A; voltage across Peltier device: 1.37 V. In the following, consider $t = 1000$ s. (a) How large would the entropy current be if the Peltier device could pump entropy directly and without any dissipation from the body of water on the left to the one on the right? The water temperatures are to be found in the second diagram. The electric data are given above. (Hint: Determine the power of the Peltier device.) (b) What is the actual entropy current out of the water in the left chamber? Neglect the effect of the mixer and all losses of heat. Entropy flows only through the Peltier device. (Hint: Determine the rate of change of the temperature of water in the left chamber using the diagram.)

Figure P.43



44. A Peltier device serves as a separating wall between two chambers in an insulated container. Hot water is poured into the left chamber, cold water into the right one (0.50 kg each). The water is stirred mechanically. A resistor is connected to the cables of the Peltier device. The lid of the container is closed. The temperatures of the two bodies of water and the voltage across the resistor are measured. The resistor has a resistance of 1.29 Ω. (a) Formulate the instantaneous form of the law of balance of entropy for one of the bodies of water. Explain. (b) Determine the rates of change of temperature of the bodies of water right at the beginning (at $t = 0$ s). (c) Estimate the entropy current through the Peltier device right at the beginning (at $t = 0$ s). (d) Determine the temperature difference between left and right and the electric power of the Peltier device for about 6 points (500 s, 750 s, …, 1750 s). Create a graph of the power as a function of the *square* of the temperature difference. (e) Explain why we should expect the result of problem d (i.e., interpret and explain what you obtained). (f) Compare the electric power to the ideal thermal power we should expect for the temperature difference between the right and the left sides (for $t = 0$ s).

Figure P.44



CHAPTER 5

THE RESPONSE OF SIMPLE MATERIALS TO HEAT

In this chapter I will present theories of the thermodynamics of some spatially uniform materials that are more complex than the one treated in Chapter 4. There we worked with a material that responds to entropy by changing its temperature only (Section 4.5). The approach taken and the basic ideas assumed to be valid are the same as those developed in the previous chapter; only the form of the constitutive relations changes. The following sections are devoted to materials undergoing simple phase change, the ideal gas, blackbody radiation, and magnetizable substances.

The case of the ideal gas is particularly interesting and important. This gas is a simple model fluid which can undergo changes of temperature and of volume. We will be able to compute adiabatic, polytropic, and more general processes undergone by this fluid. The model chosen allows only for reversible processes which means that we can actually set up a thermodynamics of non-dissipative processes. The ideas developed will be applied to blackbody radiation and to paramagnetic substances.

A more advanced and formal treatment of the subject will be given in Part III (Chapter 10). There I will develop an approach to irreversible processes in spatially uniform systems that resembles the form of theories of continuum thermodynamics but is much simpler mathematically. This will lead to a derivation of the relation between currents of entropy and of energy in heating which has been assumed to be self-evident in this part of the book (its validity is suggested to us by analogical reasoning).

5.1 MATERIALS UNDERGOING PHASE CHANGE

In the introductory sections of Chapter 4, materials undergoing phase change, i.e., melting and vaporization, were described informally. You should briefly review the experiments listed in Section 4.1 (Fig. 4.6 and Fig. 4.7), the discussion in Section 4.1.4 and the construction of *TS* diagrams in Section 4.3.3 (see Fig. 4.29). Here, I am going make the description more formal, and I will apply the simple constitutive relations for melting and freezing to an interesting dynamical case of thermal engineering—so-called latent heat storage. Still more material is found in Chapter 15.

5.1.1 Latent Entropy of Fusion and of Vaporization

The most important observations and interpretations regarding melting or vaporization are these: If we want a material to change from the solid to the liquid state or from

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_6,

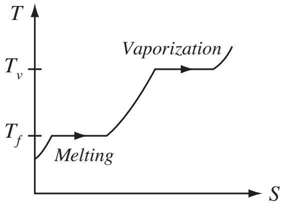


Figure 5.1: Relationship between temperature and entropy for melting or vaporization of ice and water. During the change of phase, the temperature of the body stays constant. The diagram gives only a qualitative representation of the relationships. (T_f: melting point, T_v: temperature of vaporization.)

the liquid to the gaseous phase, it has to take up entropy. Put in everyday language, to melt or to vaporize a material heat is required. The entropy communicated to a melting body or to a system undergoing vaporization is to be found within the system. Interestingly, the temperature of the material does not change during the phase change; the process is isothermal. These are the observations and interpretations that go into the construction of the *TS* diagram of H_2O going from cold ice to hot steam (Fig. 5.1; see also Section 4.3.3). The temperature at which phase change takes place is called *temperature of fusion* T_f in the case of melting or freezing and *temperature of vaporization* T_v for vaporization or condensation.

Amounts of substance during melting and vaporization. The term *melting* (*fusion*) means that a solid material is transformed into a liquid whereas *vaporization* is the transformation of a liquid into a gas. During fusion, solid disappears and liquid is produced, and during vaporization, liquid disappears and gas is produced. The reverse processes are *freezing* (*solidification*) where solid forms from liquid and *condensation* where gas changes to liquid.

Phase changes can be considered chemical reactions (Chapter 6). When one unit of solid disappears in melting, one unit of liquid is produced. If we measure the quantities of materials by the amount of substance *n* (Section 1.3.1), we can express the rates of processes by introducing *rates of production* (or destruction) of amount of substance of solid (*s*), liquid (*l*), and gas (*g*). These we call $\Pi_{n,s}$, $\Pi_{n,l}$, and $\Pi_{n,g}$. Since the rate of production of solid has the opposite sign of the rate of production of liquid during melting or fusion, and the rate of production of liquid is the negative of the rate of production of amount of gas during vaporization or condensation, we have

$$\begin{aligned} &\textit{Fusion}: && \Pi_{n,s} = -\Pi_{n,l} \\ &\textit{Vaporization}: && \Pi_{n,l} = -\Pi_{n,g} \end{aligned} \tag{5.1}$$

We know the meaning of a production rate from the production of entropy (Section 4.3.2). This meaning is transferred to the present case, only here we have negative production rates as well, i.e., *rates of destruction* of amount of substance.

Entropy in phase change. As with the heating or cooling of simple uniform materials that respond to entropy by changing their temperature (Section 4.5) we assume the processes considered here to be reversible. Entropy enters or leaves the materials easily—there are no temperature differences inside the bodies—which means that letting entropy flow in or out is not dissipative. More importantly, however, experience tells us that the processes of phase change are reversible as well. Making water out of ice takes as much heat as is emitted when water changes to ice. Therefore, we have a simple form of the law of balance of entropy: rate of change equals rate of transfer.

The constitutive relation for phase change is simple. All we need to know is how much entropy it takes to melt or to vaporize a unit of amount of a certain substance. Clearly, the quantity of entropy needed depends upon the amount of substance; double the entropy will melt or vaporize double the amount of a given material. Expressed as a dynamic relation, this means that

$$\begin{aligned} &\textit{Fusion}: && I_S = \bar{l}_f \Pi_{n,l} \\ &\textit{Vaporization}: && I_S = \bar{l}_v \Pi_{n,g} \end{aligned} \tag{5.2}$$

for melting and for vaporization, respectively. In simple words, the current of entropy of the system is proportional to the rate at which the quantity of one of the phases changes. The indices *f* and *v* stand for fusion and vaporization, respectively. So, Equ.(5.2)$_1$ tells us that the system has to be heated when liquid is produced during the solid-liquid transition and that it has to be cooled when solid is formed during the reverse liquid-solid transition. Because we assume reversibility of absorption or emission of entropy and of the phase changes themselves, we can express Equ.(5.2) in terms of rates of change of entropy as well.

Latent entropy. The factors of proportionality in Equ.(5.2), $\bar{l}_f$ and $\bar{l}_v$, are called *molar latent entropy of fusion* and *molar latent entropy of vaporization*, respectively. Molar stands for the fact that we report these values with respect to amount of substance. For example, the molar entropy of fusion of ice is about 22 J/(K · mole) which means it takes a quantity of entropy equal to 22 J/K to melt one mole of ice at 273 K. Values of entropies of fusion for different materials are listed in Table 5.1 (see Table 5.2 for values of latent entropies of vaporization). If we want to refer amounts of latent entropy to mass instead of amount of substance, we introduce *specific latent entropies* (of fusion or vaporization) that are calculated from the molar values with the help of the molar mass of the material.

Table 5.1: Latent entropy and enthalpy of fusion at 1 bar

Substance	Molar mass	Temperature of fusion	Molar Entropy of fusion	Molar Enthalpy of fusion
	M_0 / kg/mole	T_f / K	$\bar{l}_f$ / J/(K · mole)	$\bar{q}$ / J/mole
Aluminum	0.027	887	12.1	10720
Copper	0.064	1356	9.68	13120
Gallium	0.070	303	18.7	5656
Gold	0.197	1336	9.69	12943
Iron	0.056	1808	8.58	15512
Lead	0.207	600	7.94	4761
Mercury	0.201	234	10.1	2372
Platinum	0.195	2042	10.6	21645
Silicon	0.028	1693	2.17	4592
Sodium	0.023	371	7.01	2599
Tungsten	0.184	3653	9.67	35300
Water	0.018	273	22.0	6010
PCM[a]	M_0 / kg/mole	T_f / K	l_f / J/(K · kg)	q / J/kg
PCM salt[b]		300	630	188000
Sorbitol		360	513	185000
Paraffin C22-C45		330–333	570	189000

a. Phase Change Material for latent heat storage in heating and cooling applications
b. www.pcmenergy.com

The term *latent* denotes the property of entropy *not* to affect the temperature of the system during phase change. This is an old term that was coined to describe the effects of heat in isothermal processes (see Section 5.2 for another important application of the concept). Our common sense understanding of heat (entropy) is that it changes the temperature of a material, so when it does not it is termed *latent heat* in contrast to *sensible heat*.

Table 5.2: Latent entropy and enthalpy of vaporization at 1 bar

Substance	Molar mass M_0 / kg/mole	Temperature of vaporization T_v / K	Entropy of vaporization $\bar{l}_v$ / J/(K·mole)	Enthalpy of vaporization $\bar{r}$ / J/mole
Aluminum	0.027	2720	108	294000
Copper	0.064	2860	107	306000
Gallium	0.070	2500	102	255000
Gold	0.197	2950	110	325000
Iron	0.056	3000	118	354000
Lead	0.207	2020	880	1780000
Mercury	0.201	630	91	57300
Platinum	0.195	4270	105	448000
Silicon	0.028	2900	136	394000
Tungsten	0.184	5770	139	802000
Argon	0.040	87	75	6520
CO_2	0.044	195	30.9	6020
Chlorine	0.035	239	42.5	10200
Helium	0.004	4	20.5	82
Hydrogen H_2	0.002	20	45.4	908
Krypton	0.084	120	75.6	9070
Neon	0.020	27	67.6	1820
Nitrogen N_2	0.028	77	72.0	5540
Oxygen O_2	0.032	90	75.7	6820
Water	0.018	373	109	40700

5.1.2 Energy Transferred in Phase Change

The latent entropies generally change when the pressure at which phase change takes place is raised or lowered. This is particularly evident for evaporation where a gas is produced and the volume of the system changes drastically. The reason for this is that entropy drives the change of volume as well, and since this change depends upon the pressure of the fluid, so does the quantity of entropy associated with phase change at different pressures. This observation is important for understanding the role of energy in phase change, particularly in vaporization or condensation (see Chapter 15).

Enthalpy of fusion and vaporization. When a material is melted or vaporized, it has to be heated meaning that entropy is absorbed together with energy at the temperature of the system (Fig. 5.2). We have

$$\begin{aligned} I_{E,th} &= \bar{q}\,\Pi_{n,l} \\ I_{E,th} &= \bar{r}\,\Pi_{n,g} \end{aligned} \qquad (5.3)$$

for fusion and for vaporization, respectively. The factors are the energy transferred in melting ($\bar{q}$) or vaporization ($\bar{r}$) of one mole of the material. For reasons that will become clear later in Section 5.3, these quantities are called *molar enthalpy of fusion* or *molar enthalpy of vaporization*. The energy current is directly related to the flux of entropy by the temperature, so we have

$$\begin{aligned} \bar{q} &= T_f \bar{l}_f \\ \bar{r} &= T_v \bar{l}_v \end{aligned} \qquad (5.4)$$

Values of molar enthalpies are listed in Table 5.1 and Table 5.2.

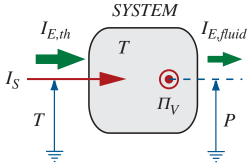


Figure 5.2: Process diagram of heating of a body at temperature T. Energy flows together with entropy. Simultaneously, energy is exchanged if the volume of the material changes. Π_V is the rate of production of volume (see Equ.(2.14)).

Energy and change of volume. Unlike the entropy added during melting or vaporization which is to be found in the new material that underwent phase change, the energy added with entropy is *not* in the system, at least not all of it. A material normally changes its volume while it goes from solid to liquid or from liquid to gas. This is particularly obvious in the case of vaporization. The process of volume change is accompanied by an exchange of energy (Fig. 5.2) as we will see more clearly in later sections of this chapter. It is important to understand that the *change of energy* of the material as a result of phase change is *not* equal to the energy transferred as a consequence of heating (or cooling). So while Equ.(5.2) holds for the change of entropy of the system as well, Equ.(5.4) does not hold for the change of the energy of the system.

When a person says that a material needs heat to melt, the expression makes sense if we mean the entropy. This point is brought home quite clearly by the altogether different role of energy in physical processes. The meaning of entropy for phase change is underlined by the values of latent entropies found in Table 5.1 and Table 5.2. We see that they do not vary that much for different substances. This is quite different for molar enthalpies which can vary by an order of magnitude or more.

5.1.3 Latent Heat Storage in Heating Systems

Phase changes play an important role in nature and machines. A simple application of the ideas presented above can be found in latent heat (entropy) storage systems that are being designed for a supporting role in heating and cooling systems. Storage of heat and cold can considerably improve the operation and efficiency of such systems ("storing cold" means readying a cold space—a space colder than the environment—that can absorb entropy).

Water is a preferred medium for storing (and transporting) entropy in domestic and industrial applications. The quantity of entropy that can be stored per unit mass per unit temperature is given by the specific entropy capacitance. Imagine that we need entropy at temperatures between – 10°C and + 10°C. If H_2O were liquid water in this range, the amount of entropy that could be stored in one kilogram of the substance would be about 300 Ct (Section 4.5). Since there is a phase change in this temperature range, the entropy taken up by 1 kg of water between – 10°C and + 10°C is actually increased by the latent entropy which is a full 1200 Ct. So with the transition from ice to water included, water would be five times as efficient as an entropy storage material in the temperature range chosen here.

This is the idea behind latent heat storage systems that make use of phase change materials (PCMs) that undergo melting and solidification.[1] A PCM has to satisfy a number of requirements to be suitable for a particular application. For one, the temperature range has to fit the application (for domestic hot water we want a temperature of fusion somewhere in the range of 50°C to 60°C). For entropy to enter or leave the system quickly enough, the conductivity of the material must be as high as possible, and the material must keep its properties for many cycles of melting and freezing. Finally we would like the latent entropy and the entropy capacitance to be high enough so that the size of a storage element can be kept reasonable.

A dynamical model for a small experimental system. Let me build a dynamical model to explain the phenomenon observed when liquid paraffin wax in copper tubes submerged in hot water cools in the environment. A small experiment demonstrates the effect of freezing of wax (Fig. 5.3).

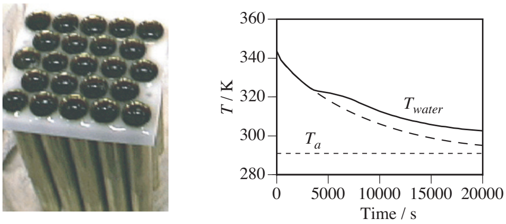


Figure 5.3: Data of temperature of water (right) surrounding tubes containing wax (left), inside an uninsulated container. The dashed line is the estimated temperature for the system if the wax did not freeze. The system is allowed to cool in the environment.

The idea for the model is quite simple. We have two bodies, wax and water, which we will treat as spatially homogenous systems. This is easily ensured in the case of the water by stirring it but will be impossible to obtain in the case of the wax. By building the PCM store from many thin copper tubes that are surrounded by water we can come closer to the ideal of homogeneous conditions. There is also some copper but the amount is kept small and its temperature will follow that of wax and water closely, so we can neglect this element in our model. As the water cools in the environment its temperature drops below that of the wax which will lose entropy to the water. Leaving out the phase change, the model is one we already know from Chapter 4. It is similar to the one in Fig. 4.49 for two bodies in thermal contact (wax and water) with an additional outflow for entropy from the second storage element (water). If we neglect entropy production due to transfer from wax to water, the central part of the model obtains the structure shown in Fig. 5.4.

The laws of balance of entropy for the bodies of wax and water are determined by the processes taking place:

---

[1] Such systems are discussed and designed in regenerative energy engineering; see Duffie and Beckman (1991), Sections 8.8 and 13.7.

$$
\begin{aligned}
\frac{dS_{wax}}{dt} &= -I_{S1} \\
\frac{dS_w}{dt} &= I_{S1} - I_{S2} + \Pi_S
\end{aligned}
\qquad \textbf{(5.5)}
$$

The body of wax is assumed to undergo reversible cooling whereas the water receives entropy from the wax and loses it to the environment. Additional entropy is produced in the water because of mechanical stirring (Fig. 5.4).

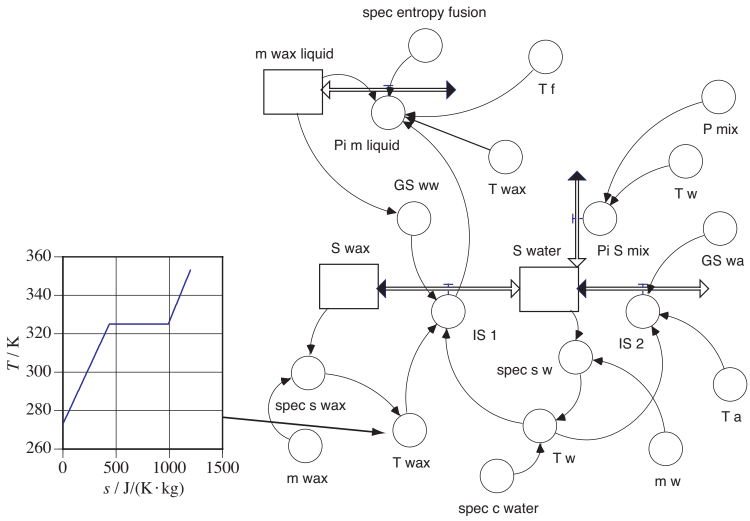


Figure 5.4: System dynamics model diagram of cooling liquid wax in a water bath (right) and *Ts* diagram for paraffin (left).

The constitutive laws for the process quantities in Equ.(5.5) are well known from previous models. They are

$$
\begin{aligned}
I_{S1} &= G_{S,ww}\left(T_{wax} - T_w\right) \\
I_{S2} &= G_{S,wa}\left(T_w - T_a\right) \\
\Pi_S &= \mathcal{P}_{mix} / T_w
\end{aligned}
$$

To calculate the temperature of the body of water, we make use of the standard relation between temperature and specific entropy known for materials having constant specific heat (Equ.(4.42)). This simple approach breaks down for the temperature of the body of wax because of the phase transition, and this is where we finally have to deal with what is new about the model of cooling of wax. Rather than using three analytic expression for the temperature-entropy relation for liquid, freezing, and solid paraffin, we can create the temperature–specific-entropy diagram for this material (see the diagram on the left in Fig. 5.4 and Example 5.2) and insert it into the modeling software. All we have to do is calculate the specific entropy of wax, $s = S/m_{wax}$, from the entropy stored in the PCM. The temperature will be determined from the *Ts* diagram.

The model is completed by the law of balance of (liquid) wax and the expression for the rate of destruction of this material:

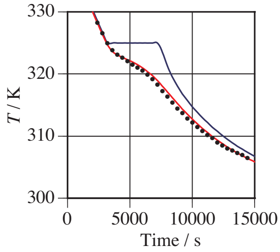


Figure 5.5: Simulation of the model in Fig. 5.4 and comparison with data (dots for the temperature of water). Solid line having a plateau: Simulated temperature of paraffin. Solid line following dots: Simulated temperature of water.

$$\frac{dm_{wax,l}}{dt} = \Pi_{m,wax,l} \qquad (5.6)$$

$$\Pi_{m,wax,l} = -\frac{1}{l_{f,wax}}\left|I_{S1}\right| \qquad (5.7)$$

We have to make sure to apply Equ.(5.7) only when the temperature of fusion has been reached, and only for as long as there is liquid paraffin.

The model works quite well (Fig. 5.5) if we make the entropy conductance $G_{S,ww}$ for transfer from wax to water dependent upon the state of the paraffin in the tubes. I chose to make it high for liquid and low for solid paraffin with a linear transition between the values dependent upon the amount of liquid wax left as the freezing progresses. The temperature of fusion chosen in the model is 52°C which agrees fairly well with data for different types of paraffin. Note the horizontal line in the temperature of wax resulting from the simulation of the model.

Actually, wax is a relatively complex substance that does not melt or freeze at a well defined temperature. Wax is a poorly defined material made up of different versions of paraffin which means that different components melt or freeze at (slightly) different temperatures. For this reason, the function having a plateau at 52°C (Fig. 5.5) does not represent the actual temperature of the wax very well. To include this effect in a simple model would have been too complicated, still the result of the simplifying assumptions are encouraging. The model is definitely good enough for prototyping.

QUESTIONS

1. Steam condenses to water. What happens with the entropy of the steam, the water, the environment?
2. Why does the temperature of the water in the graph of Fig. 5.3 have a plateau between about 3000 s and 7000 s?
3. The constitutive law for phase change, Equ.(5.2), has been formulated in terms of the rate of production or destruction of a phase involved in the process. Is the rate of production of a phase always equal to the rate of change of the amount of that phase?
4. The constitutive law for phase change, Equ.(5.2), has been formulated in terms of the exchange of entropy between system and environment. Is the current of entropy in Equ.(5.2) equal to the rate of change of entropy of the system undergoing phase change?
5. To melt ice, entropy has to be added to the system. Energy accompanies the entropy flowing in. What happens to the energy?
6. What is the specific latent entropy of fusion of paraffin according to the graph in Fig. 5.4?
7. Why might a domestic hot water store using not just water but also a phase change material make practical sense? What value of the temperature of fusion of the phase change material should we choose?
8. Why are the entropy and the enthalpy of fusion related by the temperature of fusion?

EXAMPLE 5.1. Latent entropy of fusion and vaporization of water.

Use data of the experiments reported in Fig. 4.6 and Fig. 4.7 to determine (a) the latent entropy of fusion of ice-water and (b) the latent entropy of vaporization of water-steam.

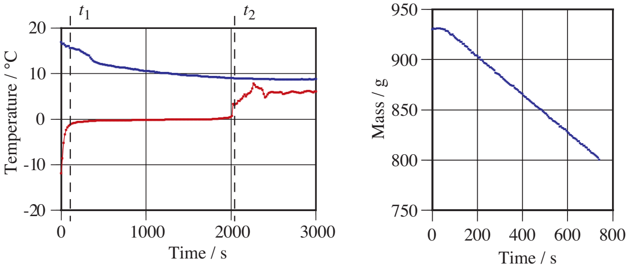


Figure Ex.1

SOLUTION: (a) We estimate that ice in the test tube is melting from about 100 s to 2000 s (see the diagram on the left in Fig. Ex.1). It probably starts a little earlier than the time when the thermometer in the ice shows 0°C (the thermometer is at the center of the cylinder of ice). During this period, the temperature of the water (and therefore also of the glass container) decrease from 15.7°C to 9.0°C. Entropy is produced because of stirring. The balance of entropy of water and glass container is

DATA

Melting of ice:

$m_{water} = 0.911$ kg
$m_{ice} = 0.091$ kg
$m_{glass} = 0.193$ kg
$P_{mixer} = 1.2$ W

Vaporization of water:

$\mathcal{P}_{heater} = 438$ W
$T_v = 98.1$°C

$$\Delta S_{w+g} = S_{e,\,ice} + S_{prod}$$

where $S_{e,ice}$ is the entropy lost by the water to the ice which equals the entropy received by the ice (if we neglect entropy production due to heat transfer). The change of entropy of water and glass and the entropy produced are calculated from

$$\begin{aligned} \Delta S_{w+g} &= \left(m_w \kappa_w + m_g \kappa_g\right)\left(T_{w2} - T_{w1}\right) \\ &= (0.911 \cdot 14.7 + 0.193 \cdot 2.9) \cdot (9.0 - 15.7)\,\mathrm{J/K} = -93.5\,\mathrm{J/K} \\ S_{prod} &= \frac{\mathcal{P}_{mix}}{T_w}\Delta t = \frac{1.2}{273 + 12} 1900\,\mathrm{J/K} = 8.0\,\mathrm{J/K} \end{aligned}$$

This yields the entropy lost by the water to the body of ice during melting:

$$S_{e,\,ice} = \Delta S_{w+g} - S_{prod} = -101.5\,\mathrm{J/K}$$

The ice received 101.5 J/K of entropy. This makes the specific entropy of fusion equal to

$$l_{f,\,ice} = \frac{1}{m_{ice}}\left|S_{e,\,ice}\right| = \frac{101.5}{0.091}\frac{\mathrm{J}}{\mathrm{K \cdot kg}} = 1110\frac{\mathrm{J}}{\mathrm{K \cdot kg}}$$

which is about 10% smaller than the value found in tables (Table 5.1).

(b) From the graph in Fig. Ex.1.1 (right) we read the rate of change of mass of the body of water being heated and vaporized. This value equals – 0.189 g/s. With a rate of production of entropy equal to Π_S = 438 W / (273.15 + 98.1) K = 1.18 W/K, we obtain

$$l_{v,\,water} = \frac{\Pi_S}{\left|dm_w/dt\right|} = \frac{1.18}{0.189 \cdot 10^{-3}}\frac{\mathrm{J}}{\mathrm{K \cdot kg}} = 6240\frac{\mathrm{J}}{\mathrm{K \cdot kg}}$$

which is slightly higher than tabulated values for vaporization of water at 100°C (Table 5.2).

EXAMPLE 5.2. Constructing a *Ts* diagram for paraffin.

DATA *for paraffin:*

$\kappa_{solid} = 8$ J/(K^2·kg)
$\kappa_{liquid} = 7$ J/(K^2·kg)
$l_f = 570$ J/(K·kg)
$T_{f,min} = 50$°C
$T_{f,min} = 55$°C

Construct a temperature–specific-entropy diagram for paraffin using the following data. Solid and liquid paraffin have similar entropy capacitances (see the table of values on the side). The material melts between 50°C and 55°C with a specific entropy of fusion of about 570 J/(K·kg).

SOLUTION: Let us choose a value of 0 J/(K·kg) for the specific entropy of the material at 0°C (273 K). The temperature will increase (almost linearly) with entropy up to 323 K. At this point, the specific entropy should be

$$s(323\,\mathrm{K}) = 0\frac{\mathrm{J}}{\mathrm{K\cdot kg}} + 8\cdot(323-273)\frac{\mathrm{J}}{\mathrm{K\cdot kg}} = 400\frac{\mathrm{J}}{\mathrm{K\cdot kg}}$$

The simplest approximation to a function $T(s)$ for melting with increasing temperature is a linear function, so we have a specific entropy of (400 + 570) J/(K·kg) = 970 J/(K·kg) at 328 K. From there, the temperature rises again (almost) linearly with entropy so that

$$s(373\,\mathrm{K}) = 970\frac{\mathrm{J}}{\mathrm{K\cdot kg}} + 7\cdot(373-323)\frac{\mathrm{J}}{\mathrm{K\cdot kg}} = 1320\frac{\mathrm{J}}{\mathrm{K\cdot kg}}$$

The *Ts* diagram representing this data is shown in the graph of Fig. Ex.2. Compare this to the diagram in Fig. 5.4.

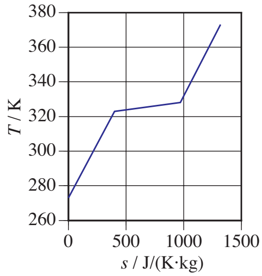


Figure Ex.2

EXAMPLE 5.3. Freezing water in a freezer.

One liter of water (which already has a temperature of 0°C) is frozen in a freezer which we assume to function as an ideal heat pump. The temperature in the freezer has to be maintained at a temperature of 0°C. How much entropy is extracted from the water, and how much energy is needed to emit this entropy to the kitchen at a temperature of 22°C?

SOLUTION: The amount of entropy emitted when water is turned into ice is determined by the constitutive law of fusion:

$$\begin{aligned} S_e &= n\bar{l}_f = m\bar{l}_f / M_0 \\ &= \frac{1.0\,\mathrm{kg}\cdot 22.0\,\mathrm{J/(mole\cdot K)}}{0.018\,\mathrm{kg/mole}} = 1220\,\mathrm{J/K} \end{aligned}$$

This amount of entropy flows into the freezer and has to be removed. The energy needed to operate the freezer while the water is freezing is equal to the energy E_{th} needed to lift this amount of entropy from a temperature of 0°C to one of 22°C:

$$\begin{aligned} E_{th} &= (T_2 - T_1)S_e \\ &= (295\,\mathrm{K} - 273\,\mathrm{K})\cdot 1220\,\mathrm{J/K} = 26.8\,\mathrm{kJ} \end{aligned}$$

5.2 THERMOFLUID PROCESSES OF THE IDEAL GAS

In terms of the concepts introduced so far, the problem of thermodynamics is the determination of the currents and the rates of generation of entropy. We have approached this problem by discussing some very simple constitutive laws, namely those governing the heating of ideal bodies at constant volume (Section 4.5), overall entropy transfer (Section 4.6), and the change of phase of a substance such as water (Section 5.1). By restricting our attention to processes at constant volume we have essentially excluded gases. In this and the following sections we shall extend the analysis to bodies which can change their volumes and their temperatures. The *ideal gas* and *blackbody radiation* (Section 5.4) will serve a examples of such materials.

We begin by formulating the laws of balance pertaining to fluids that can undergo heating and volume change and add the relations for energy transfers having to do with these processes. Then we continue by stating a first constitutive law, the *thermal equation of state* of the ideal gas, which relates the pressure of the fluid to its temperature and its volume. Heating will be represented by a constitutive relation which introduces the *latent entropy* and the *entropy capacitance*, and volume change is described simply by the production rate of volume. As we will see, the model allows only for *reversible processes* of the ideal gas.

5.2.1 Laws of Balance and Energy Relations in Thermofluid Processes

A body of air is more interesting than a stone from the viewpoint of thermodynamics since it couples thermal processes of heating or cooling to fluid (or mechanical) processes of expansion or compression. This coupling leads to new effects that can be understood if we manage to clearly distinguish the underlying processes (Fig. 5.6).

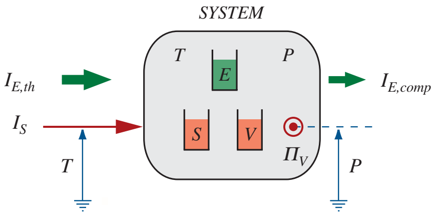


Figure 5.6: Process diagram of an ideal fluid undergoing heating or cooling and compression or expansion. Heating means entropy transfer and compression denotes destruction of volume. Π_V is the production rate of volume.

Laws of balance for ideal fluids. As always, we need to formulate the laws of balance pertaining to the processes a system can undergo. Since a simple gas couples thermal and fluid phenomena, we should expect two expressions, one for the balance of entropy and the other for the balance of volume.

When we deal with entropy we have to be clear how we want to handle possible irreversibilities. In the case of a gas, there are two possible sources of entropy production. The first is the spreading of entropy through the body as a result of heating or cooling; the second is friction in the fluid as it undergoes compression or expansion. Since we want to model the simplest thermal processes, i.e., spatially uniform ones, we again assume that heat can spread easily through the body making entropy production due to transfer equal to zero. The case of internal friction is handled similarly. It is quite acceptable to assume that friction in a body of air is small as it is compressed or expanded. In summary, we assume that

$$\Pi_{S,heat\,transfer} + \Pi_{S,friction} = 0 \tag{5.8}$$

which leads to the law of balance of entropy for reversible processes:

$$\dot{S} = I_S \tag{5.9}$$

Only heating or cooling can change the entropy of the model gas we are going to consider here.

The balance of volume is rather simple as well. In this chapter we will neglect transfer of matter into or out of a system, so the systems chosen are made of fixed amounts of substance. Since the material is assumed to be compressible, its volume is not conserved. The volume changes due to creation (expansion of the gas) or destruction (compression) for which we introduce a production rate Π_V. Therefore:

$$\dot{V} = \Pi_V \tag{5.10}$$

We also have to consider the balance of energy—remember that we make energy responsible for the coupling of processes. Since a simple gas undergoes two types of processes we should expect two types of energy transfer, one associated with heating and the other with compression. Therefore, the law of balance of energy includes two expressions for energy fluxes:

$$\dot{E} = I_{E,th} + I_{E,comp} \tag{5.11}$$

Energy relations. $I_{E,th}$ denotes the energy flux that accompanies the entropy transfer in heating and cooling and $I_{E,comp}$ is the rate at which energy is transferred as a result of production of volume. According to Chapters 4 and 2, these fluxes are

$$I_{E,th} = T\, I_S \tag{5.12}$$

$$I_{E,comp} = -P\, \Pi_V \tag{5.13}$$

where T and P are the temperature and the pressure of the gas, respectively.[2] The negative sign in Equ.(5.13) tells us that the body of gas receives energy when it is compressed (negative Π_V) and it loses energy when it expands (positive Π_V).

This completes the generic laws and the generic energy relations. The rest of the model of the thermofluid processes of the ideal gas must come from constitutive relations.

5.2.2 Heating of an Ideal Fluid

As before, heating means absorption of entropy by a body; cooling means that the body loses entropy; the terms heating and cooling do not refer to any other circumstances. So the question we are dealing with is how a gas responds to entropy. Everyday experience tells us that a typical fluid either expands or gets warmer when its entropy increases.[3] The type of fluid considered will be an ideal one where ideal is defined by Equ.(5.8) and therefore by Equ.(5.9). There is no entropy production in the fluid, and the entropy current in heating or cooling equals the rate of change of entropy of the body.

Isothermal heating of an ideal fluid. Let us now turn to the constitutive problem of the heating of a fluid such as the ideal gas (whose other properties we will define in

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[2] The derivation of Equ.(5.13) suggests that we look upon compression and expansion of a body of gas as a fluid (hydraulic) process. We may just as well consider it a mechanical process where the transfer of momentum through the body is accompanied by the motion of its surface (Chapter 3). The result for energy transfer, Equ.(5.13), is the same.

[3] A fluid need not expand when it takes up entropy. A notable and most important exception to the rule is water which contracts if it is heated at temperatures between 0°C and 4°C. In this chapter we will consider only the ideal gas that expands upon heating.

Section 5.2.3). In Section 4.3.3 we discussed the problem of heating or cooling of a fluid at constant temperature. A fluid can be expanded or compressed isothermally if it is heated or cooled at the appropriate rate. The entropy therefore has the effect of changing the volume of the body. It does not do what we expect heat to do: it does not increase the temperature of the body. For this reason the term *latent heat* was coined to denote the heat absorbed in an isothermal process. It is instructive to hear how this name was used more than 180 years ago by J. Ivory:[4]

> The absolute heat which causes a given rise of temperature, or a given dilatation, is resolvable into two distinct parts; of which one is capable of producing the given rise of temperature, when the volume of the air remains constant; and the other enters into the air, and somehow unites with it while it is expanding … . The first may be called the heat of temperature; and the second might very properly be named the heat of expansion; but I shall use the well known term, latent heat, understanding by it the heat that accumulates in a mass of air when the volume increases, and is again extricated from it when the volume decreases.

Here we will formalize the definition of *latent entropy*. It is the factor Λ_V which relates rates of change of entropy content to rates of change of volume, i.e., it tells us how much entropy is needed to let a gas expand at constant temperature:

$$\dot{S} = \Lambda_V \dot{V} \tag{5.14}$$

We will call this new quantity the *latent entropy with respect to volume*. It tells us how much entropy we need to let a body expand by one unit of volume. Since we are considering ideal fluids, the rate of change of entropy equals the flux of entropy in heating which means that:

$$I_S = \Lambda_V \dot{V} \tag{5.15}$$

It is instructive and useful to exhibit the process of isothermal heating in the *TV* diagram (Fig. 5.7).[5]

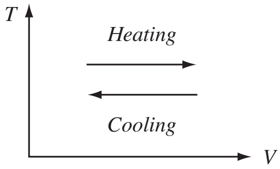

Figure 5.7: *TV* diagram of isothermal heating or cooling of a compressible fluid. In most cases, the volume of a fluid increases if it is heated at constant temperature (the latent entropy is positive). However, there are exceptions, such as water in the temperature range 0 – 4°C (here, the latent entropy is negative)..

We can easily calculate the amount of entropy exchanged in an isothermal process, or the change of the entropy content, by integrating the current of entropy from an initial point in time t_i to a final point t_f:

$$S_e = \int_{t_i}^{t_f} I_S \, dt = \int_{t_i}^{t_f} \Lambda_V \dot{V} \, dt \tag{5.16}$$

or

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[4] J. Ivory (1827), quoted by Truesdell (1980), p. 17. Much more information regarding the caloric theory may be found in Fox (1971).

[5] The use of *TV* diagrams was customary in the original development of thermodynamics. Today's custom of using *PV* diagrams does not make nearly as much sense. To use two fluid (or mechanical) variables, i.e., pressure and volume, for thermodynamics might give us the mistaken impression that a science of heat does not have to make use of thermal quantities. The old choice of temperature and volume was fortunate since it is the only one that allows for a complete mathematical theory of thermodynamics of fluids including water with its anomaly. See Truesdell (1979) and Truesdell and Bharatha (1977) for a detailed discussion of this matter.

$$S_e = \int_{V_i}^{V_f} \Lambda_V \, dV \tag{5.17}$$

We have not really solved the constitutive problem yet. The burden of calculating the current has been placed on the determination of a new quantity, namely the latent entropy. We can calculate the process of heating at constant temperature only if we know this constitutive quantity. We could try to measure it in a manner analogous to what we did for the entropy capacitance of incompressible materials (Section 4.5.3). In practice, however, it is very difficult to measure the latent entropy of gases since they take up very little entropy in comparison to measuring devices and containers. For this reason, it would be nice if we could find new ways of dealing with the constitutive problem. Fortunately, the relationship between entropy and the power of a fall of entropy through a temperature difference, which we have not exploited yet, introduces severe restrictions on the constitutive relations. These restrictions will reduce the burden of measurement: we will be able to determine the latent entropy of the ideal gas using theoretical arguments (see Section 5.2.6).

Heating of the ideal gas at constant volume. J. Ivory spoke of two effects of heating. If you add heat to a body, either the volume or the temperature (or both) will change. Here, we will investigate the second possibility, namely a change of temperature alone. This can happen only if the volume of the body is forcibly kept constant. With solids or liquids this condition is automatically satisfied to a high degree. Gases have to be put in an airtight container.

As in the case of heating of solids or liquids, we introduce the *entropy capacitance at constant volume*, i.e., the coefficient K_V which relates rates of change of the entropy content to rates of change of temperature:

$$\dot{S} = K_V \dot{T} \tag{5.18}$$

Here we refer explicitly to the condition of *heating at constant volume*, since the volume of a gas does not stay nearly constant as in the case of solids or liquids. Again, we assume we are dealing with an ideal fluid, so:

$$I_S = K_V \dot{T} \tag{5.19}$$

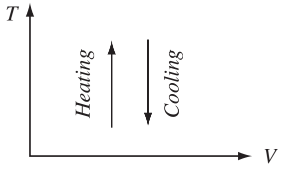

Figure 5.8: *TV* diagram of isochoric heating or cooling of a compressible fluid.

As in the case of isothermal heating, it is instructive to represent the process in a *TV* diagram (Fig. 5.8). In general the entropy capacitance is a function of both the volume and temperature of the body. We can determine the amount of entropy exchanged during heating at constant volume:

$$S_e = \int_{t_i}^{t_f} I_S \, dt = \int_{t_i}^{t_f} K_V \dot{T} \, dt \tag{5.20}$$

or

$$S_e = \int_{T_i}^{T_f} K_V \, dT \tag{5.21}$$

Direct measurements of the entropy capacitance at constant volume of gases are not so simple to do since the values are rather small compared to those for the measuring apparatus. We will be able to solve the constitutive problem in a combination of theoretical and experimental steps (Section 5.2.8). Theory allows us to relate the quantities we seek to others that might be simpler to measure.

The general process of heating of an ideal fluid. In general, a body which is heated undergoes changes of volume and of temperature simultaneously. For this reason, the entropy content must depend on both the volume and the temperature. Its rate of change must depend upon the rates of change of the independent variables. In other words,

$$\dot{S} = \Lambda_V \dot{V} + K_V \dot{T} \tag{5.22}$$

The coefficients are the latent entropy with respect to volume and the entropy capacitance at constant volume, respectively. For ideal fluids the rate of change of entropy equals the entropy current in heating or cooling, so we have:

$$I_S = \Lambda_V \dot{V} + K_V \dot{T} \tag{5.23}$$

We shall see in one of the following sections (Section 5.2.7) how this law can be exploited in the case of adiabatic processes undergone by the ideal gas, without us even knowing the form of the constitutive quantities. This will prove an important step in solving the constitutive problem of the ideal gas.

5.2.3 The Thermal Equation of State of the Ideal Gas

The ideal gas is a system which can change its volume and temperature. These two variables are related to a third property of the gas, namely its pressure. In Section 4.3.1, we encountered the *law of Gay-Lussac* which is obeyed by dilute gases. It states that the pressure of the fluid is a linear function of temperature if it is heated at constant volume. One finds that such gases have another simple property. Experiments demonstrate that the pressure and volume of a gas such as air at room temperature are inversely proportional if the temperature is kept constant (Fig. 5.9):

$$PV = constant \tag{5.24}$$

This relation is called the *law of Boyle and Mariotte*. The laws of Gay-Lussac and of Boyle and Mariotte together define the *ideal gas* as the fluid having the following *thermal equation of state*:[6]

$$PV = nRT \tag{5.25}$$

Here, $R = 8.314$ J/(mole · K) is the *universal gas constant*, and n is *the amount of substance* measured in moles.[7]

The *amount of substance* comes into the equation of state of the ideal gas in the following way. It is found that the law holds with a single (universal) value of the gas constant if certain mass ratios of different gases are used. For example, 16 g of oxygen gas turn out to be equivalent to 1 g of hydrogen gas. These amounts also turn out to be chemically equivalent in the sense that simple fractions or multiples of these numbers occur in chemical reactions using up all of the reactants. Since the amount of substance is the fundamental measure of how much stuff is participating in chemical reactions, the coefficient n appearing in the equation of state also measures the amount of substance.

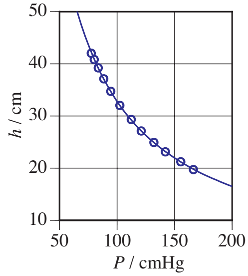

Figure 5.9: Relation between volume and pressure of air at constant temperature. The air is inside a cylinder with mercury as the piston. h is the height of the air column (proportional to volume) and P is measured in cm mercury column. The function fitted through the data points is the expected hyperbola (see Equ.(5.24)).

Gases obeying both the laws of Gay-Lussac and of Boyle and Mariotte do not really exist in nature. Rather, a real gas approximates the behavior of an ideal fluid called the *ideal gas* if its temperature is high and its density low. What can be understood as sufficiently high or low needs to be determined by experience. Basically, gases follow the ideal law for temperatures which are high compared to the point at which they liquefy. The material at the center of the Sun behaves as an ideal gas despite its high density.

It is often useful to write the equation of state of the ideal gas in terms of density instead of volume. We express the volume of the body by its density and its mass: $V = m/\rho$. Further, we have the following relationship between the mass and the amount of substance of the fluid: $m = M_0 n$. Here, M_0 is the *molar mass* (mass per unit amount of substance) of the gas. Using these relationships, the equation of state of the ideal gas becomes

$$P = \frac{R}{M_0}\rho T \tag{5.26}$$

5.2.4 Transformation of the Constitutive Relation for Heating of the Ideal Gas

In Section 5.2.2, the constitutive relation for the response of an ideal fluid to entropy was formulated by considering the general case of a combination of heating at constant volume and at constant temperature. In other words, we used temperature and volume as the independent variables of the formulation. Since a fluid has a third important property, i.e., its pressure, we could write the constitutive relation with the help of pressure and temperature. Since we have a relation between P, V, and T for the ideal gas (Equ.(5.25)), we can solve the problem for this fluid.

We would like to introduce the expression for the heating (Equ.(5.23)) in a form involving pressure and temperature, instead of volume and temperature. In practice, heating often occurs at constant pressure, which makes the new form particularly use-

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6. Proof of Equ.(5.25): Since P is proportional to $1/V$ at constant T (Boyle's relation), the product PV is a constant that depends only on the temperature of the gas:

$$PV = f(T)$$

Here, $f(T)$ is an unspecified function. Also, since P is proportional to T at constant volume, P/T is a constant which depends on the volume only. Therefore, P/T is some other function $g(V)$ of the volume:

$$P/T = g(V)$$

If we divide the first equation by T and multiply the second one by V we get

$$PV/T = f(T)/T$$
$$PV/T = Vg(V)$$

This implies that the quantity PV/T is a function of T alone and a function of V alone. Therefore, it cannot be a function of either T or V, which means that it is constant: $PV/T =$ constant.

7. See Chapter 6 for more details on the subject of the amount of substance.

ful for some applications:

$$I_S = \Lambda_P \dot{P} + K_P \dot{T} \tag{5.27}$$

The new constitutive quantities are called the *latent entropy with respect to pressure* Λ_P, and the *entropy capacitance at constant pressure* K_P, respectively. For the ideal gas, it is simple to relate them to quantities involving the volume of the body. We derive this relationship with the help of the time derivative of the equation of state:

$$P\dot{V} + V\dot{P} = nR\dot{T} \tag{5.28}$$

This allows us to replace the time derivative of the volume in Equ.(5.23):

$$\begin{aligned} I_S &= \Lambda_V \frac{1}{P}\left(nR\dot{T} - V\dot{P}\right) + K_V \dot{T} \\ &= -\Lambda_V \frac{V}{P}\dot{P} + \left(\Lambda_V \frac{nR}{P} + K_V\right)\dot{T} \end{aligned} \tag{5.29}$$

If we compare this to the expression of the heating involving the pressure, Equ.(5.27), we find that

$$\Lambda_P = -\Lambda_V \frac{V}{P} \tag{5.30}$$

$$K_P = \frac{nR}{P}\Lambda_V + K_V \tag{5.31}$$

This result demonstrates that knowledge of both entropy capacitances is equivalent to knowing the capacitance at constant volume and the latent entropy with respect to volume. Since the measurement of the (ratio of the) entropy capacitances will prove simpler than that of the latent entropy in many cases, the relationships just derived are of particular importance.

5.2.5 Energy Exchanged in Isothermal Compression

There is one more important element of preparation before we can tackle the constitutive problem of the ideal gas in Section 5.2.6. We know from fluids and mechanics how to find the energy exchanged during compression or expansion of an ideal fluid. The general form is given by Equ.(5.13). From what we already know about the ideal gas we can find the energy exchanged in *isothermal* compression or expansion. We use the law of balance of volume (Equ.(5.10)) and the equation of state of the ideal gas (Equ.(5.25)) and insert both in Equ.(5.13):

$$I_{E,comp} = -\frac{nRT}{V}\dot{V}$$

This can be integrated over a period of time to yield

$$E_{comp} = -\int_{t_i}^{t_f} \frac{nRT}{V}\dot{V}\,dt = -nRT\int_{V_i}^{V_f} \frac{1}{V}dV$$

and finally

$$E_{comp} = -nRT \ln\left(\frac{V_f}{V_i}\right) \tag{5.32}$$

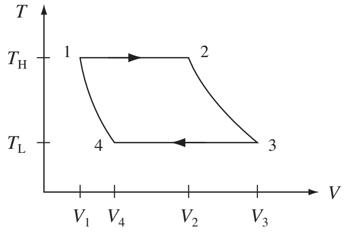
Note that the result does not depend on the absolute values of the volumes involved but rather on the ratio of final to initial volume. A doubling of the volume of one mole of a gas at room temperature means that about 1.7 kJ are emitted by the gas to the environment.

5.2.6 The Constitutive Problem of the Ideal Gas

The ideal gas is described by three functions, pressure (Equ.(5.25)), latent entropy (Equ.(5.14)), and entropy capacitance (Equ.(5.18)). We know the first of these three relations, but not the latter two. We can gain additional information on the latent entropy based upon theoretical considerations alone. In this subsection we shall give a brief account of the theory along the lines of what Carnot did some 180 years ago. The entropy capacitances will be found after considering adiabatic processes in Section 5.2.7. When we have finally solved the complete constitutive problem of the ideal gas, we will be able to discuss in detail the operations undergone by a fluid serving as the driving agent in a heat engine (Section 5.3).

By applying the relations developed up to this point to the operation of a Carnot engine (see Section 4.4.3 and Fig. 4.34), we will be able to determine the latent entropy of the ideal gas. For this purpose we have to discuss how the ideal gas is used as the driving agent of a Carnot engine. Absorbing entropy from a furnace at constant temperature is achieved by letting the ideal gas *expand isothermally* (step 1, from points 1 to 2 in Fig. 5.10). The second step must be an *adiabatic expansion*, which serves to lower the temperature of the gas to equal that of the cooler. During step 3 the entropy absorbed must be discharged. This is done by *compressing the fluid isothermally*. Finally, in step 4 (between points 4 and 1), the gas is *compressed adiabatically*. As a consequence, the temperature of the working agent is raised back to its initial value. The four-step cycle just outlined is called a *Carnot cycle*.

Figure 5.10: Carnot cycle of the ideal gas. The curved lines are the adiabats. The cycle runs between a furnace at high temperature T_H and a cooler at lower temperature T_L.



To obtain a restriction on the constitutive quantities of the ideal gas we proceed as follows. (This pretty much corresponds to what Carnot did in his theory of heat engines.) Consider a Carnot cycle operating with a very small difference of the temperatures between the furnace and the cooler:

$$\Delta T = T_H - T_L << T_H \tag{5.33}$$

In this case the adiabats of the ideal gas in Fig. 5.10 are very short, which means that they do not contribute to the exchange of energy in the *mechanical* process. For this reason we do not have to know more about adiabatic processes yet. The energy exchanged in compression and expansion in such a Carnot cycle is determined by the isotherms alone. According to Equ.(5.32), this quantity must be equal to

$$\begin{aligned} E_{comp} &= -nR(T+\Delta T)\ln\left(\frac{V_2}{V_1}\right) + nRT\ln\left(\frac{V_3}{V_4}\right) \\ &\approx -nR\Delta T\ln\left(\frac{V_2}{V_1}\right) \end{aligned} \tag{5.34}$$

The last step is a consequence of the fact that for a Carnot cycle having short adiabats the corresponding volumes must be nearly equal (Fig. 5.10), i.e., $V_3 = V_2$, and $V_4 = V_1$. From what we know about the motive power of a Carnot engine (Chapter 4) we can say that the energy released by the engine in one cycle is given by

$$E_{th} = -(T_L - T_H)S_e = -\Delta T\, S_e \tag{5.35}$$

If we combine Equations (5.34) and (5.35), we see that the entropy absorbed from the furnace must be

$$S_e = nR\ln\left(\frac{V_2}{V_1}\right) \tag{5.36}$$

On the other hand, the entropy absorbed in the isothermal expansion, S_e, is equal to the integral of the latent entropy over the volume, Equ.(5.17). This is possible only if the *latent entropy of the ideal gas* is given by

$$\Lambda_V = \frac{nR}{V} \tag{5.37}$$

In summary, the theory of thermodynamics—the relationship between entropy and energy—determines one of the constitutive quantities of the ideal gas. Note that Λ_V is proportional to the molar density (concentration) of the gas.

5.2.7 Adiabatic Processes of the Ideal Gas

In Section 4.3.3 we saw that the temperature of a compressible fluid can be raised by compression alone without heating. Processes in which heating is absent are called *adiabatic*. They play a major role in natural and man-made phenomena such as the propagation of sound, the transport of heat by convection in the Earth's atmosphere, or cycles in heat engines and refrigerators. Since adiabatic processes allow us to measure a constitutive quantity of the ideal gas, namely, the ratio of its entropy capacitances, we will be able finally to compute all quantities determining its behavior (Section 5.2.8).

Description of adiabatic motion. If you suddenly compress air inside a cylinder, its temperature increases; if the air is expanded, its temperature decreases (Fig. 5.11). These changes occur without heating or cooling which can be achieved by insulating the cylinder against the flow of entropy.

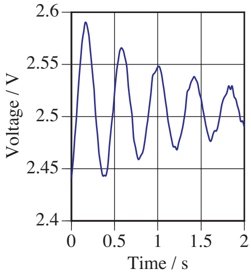


Figure 5.11: Voltage of a sensitive resistive thermometer as function of time. The thermometer is in air that is compressed and expanded rhythmically. A glass cylinder is fitted onto the neck of a large beaker and moves up and down on the air cushion inside the beaker. The motion is so fast that the air does not have time to be heated or cooled. The experiment is an example of Rueсhardt's experiment (see Torzo et al., 2001).

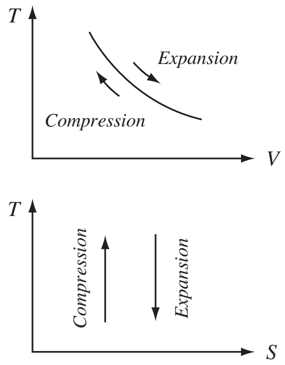


Figure 5.12: *TV* and *TS* diagrams of adiabatic compression and expansion. The term *adiabatic* means that entropy cannot be transmitted across the boundaries of the body. The temperature of most fluids, such as the ideal gas, decreases as a consequence of adiabatic expansion. The curve in the *TV* diagram is typical of the ideal gas.

The term *adiabatic* simply means that *no entropy has been exchanged* between the body and its surroundings. In other words, entropy currents across the surface of the system are equal to zero. It is convenient to display adiabatic processes in a *TV* diagram or in the *TS* diagram (Fig. 5.12, see also Chapter 4, Fig. 4.26). The temperature of the ideal gas rises if the fluid is compressed and it drops when the fluid is allowed to expand. Remember that the material can undergo reversible processes only. For this reason, the amount of entropy stored in the gas remains constant while the temperature changes. We have to conclude that the curve representing adiabatic compression in the *TS* diagram is a vertical arrow pointing up. The reverse, adiabatic expansion, results in a drop of temperature at constant entropy. Therefore, the representative curve in the *TS* diagram will be a vertical arrow pointing down.

How does this change arise? Our simple descriptions of isochoric and isothermal processes contain the seeds of an understanding of adiabatic operations. In real life, heating at constant volume and heating at constant temperature usually do not occur separately. The entropy content of a body changes when its volume and temperature change. Part of the added entropy increases the temperature, and part of it is changes the volume. In adiabatic changes, however, entropy does not cross the boundary of the body. Therefore the entropy normally emitted in the isothermal compression of the gas cannot leave the system. As a consequence, it raises the temperature. In somewhat oversimplified terms, we could say that in adiabatic compression some latent heat has been “converted” into sensible heat. (Do not take this literally; there only is one type of entropy inside a body!) A better way to explain the phenomenon graphically may be to say that *the entropy of the gas is squeezed into a smaller space*.

We can give a mathematical statement of the fact that heat does not cross the surface of the system under consideration. The current of entropy vanishes, which means that

$$I_S = 0 \tag{5.38}$$

which according to Equ.(5.23) is equivalent to

$$0 = \Lambda_V \dot{V} + K_V \dot{T} \tag{5.39}$$

or

$$\frac{dT}{dV} = -\frac{\Lambda_V}{K_V} \tag{5.40}$$

This is the fundamental equation of adiabatic change of ideal fluids including the ideal gas. In principle, we can solve the differential equation if we know the ratio of the latent entropy and the entropy capacitance of the fluid.

Solution to the problem of adiabatic motion of the ideal gas. We can derive the theory of adiabatic changes for the ideal gas. As a first step, the expression for the entropy current has to be transformed so that it contains the two entropy capacitances. The equation of state is used to eliminate the rate of change of temperature in Equ.(5.23). From Equ.(5.28) we obtain

$$\dot{T} = T\left(\frac{\dot{P}}{P} + \frac{\dot{V}}{V}\right) \tag{5.41}$$

Now, the entropy current takes the following form:

$$
\begin{aligned}
I_S &= \Lambda_V \dot{V} + K_V \dot{T} = \Lambda_V \dot{V} + K_V T\left(\frac{\dot{P}}{P} + \frac{\dot{V}}{V}\right) \\
&= T\left[K_V \frac{\dot{P}}{P} + \left(K_V + \Lambda_V \frac{V}{T}\right)\frac{\dot{V}}{V}\right]
\end{aligned}
\tag{5.42}
$$

Using the relationship between K_P and K_V, Equations (5.30) and (5.31), we conclude that

$$
I_S = T\left[K_V \frac{\dot{P}}{P} + K_P \frac{\dot{V}}{V}\right] \tag{5.43}
$$

If we now apply the condition of adiabatic change, Equ.(5.38), we get a simple differential equation for pressure and volume. With the *ratio of the entropy capacitances* defined by

$$
\gamma \equiv K_P / K_V \tag{5.44}
$$

this equation takes the form

$$
\frac{\dot{P}}{P} + \gamma \frac{\dot{V}}{V} = 0 \tag{5.45}
$$

Naturally, the equation of adiabatic change can be integrated only if the constitutive quantities themselves, or their ratio γ, are known for the ideal gas. Fortunately, we have independent information concerning the ratio of the entropy capacitances. Different types of measurements, which do not involve measuring amounts of entropy, all indicate that *for the ideal gas this ratio must be constant*:

$$
\gamma = constant \tag{5.46}
$$

Also, this constant is larger than 1, which means that more entropy is needed to raise the temperature of the ideal gas by one degree in an isobaric process than in an isochoric one. An example of how to measure this important ratio is presented in Section 5.2.9. More important still is the propagation of sound in the ideal gas (Example 5.5) which gives the same result. Now the solution of the problem of *adiabatic motion of the ideal* gas is very simple. Integration of the differential equation gives the *law of Poisson and Laplace*:

$$
PV^{\gamma} = constant \tag{5.47}
$$

Using the thermal equation of state of the ideal gas, $PV = nRT$, this relation can be written with different variables:

$$
P^{1-\gamma}T^{\gamma} = constant \tag{5.48}
$$

or

$$
TV^{\gamma-1} = constant \tag{5.49}
$$

Remember that all of these equations hold *for the ideal gas only*. The curves representing adiabatic change in a pressure-volume (*PV*) diagram, which are usually found in books on thermodynamics, are derived from the form just calculated. For different types of fluids there may be completely different adiabats which do not even faintly resemble those for the ideal gas (Fig. 5.13). *Existence and form of the adiabats are constitutive properties*. Since the *adiabatic exponent* $\gamma > 1$, adiabats of the ideal gas in the *PV* diagram are steeper than isotherms.

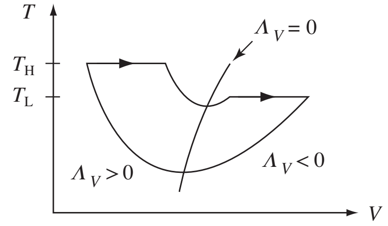


Figure 5.13: A strange Carnot cycle resulting for a fluid having an anomaly such as water (curved parts are adiabats). For water, the latent entropy is positive above 4°C and negative between 0°C and 4°C. At the maximum density at 4°C, $\Lambda_V = 0$. When $\Lambda_V < 0$, entropy is emitted when the body expands at constant temperature. See Thomsen and Hartka (1962).

5.2.8 Determining the Entropy Capacitances of the Ideal Gas

In Section 5.2.6 we determined the latent entropy of the ideal gas on the basis of theoretical considerations. The missing piece of information, i.e., the entropy capacitances of the ideal gas, can be calculated if we know their ratio. Above in Section 5.2.7, we have found that this ratio must be constant and that it can be measured in a number of ways. According to the results of Sections 5.2.4 and 5.2.6, Equations (5.30), (5.31) and (5.37), we obtain

$$K_V = n\frac{R}{\gamma - 1}\frac{1}{T} \tag{5.50}$$

$$K_P = n\frac{\gamma R}{\gamma - 1}\frac{1}{T} \tag{5.51}$$

From this the molar capacitances can be calculated. Note that the entropy capacitances of the ideal gas are inversely proportional to its temperature.[8] There is a simple relationship between the molar capacitances:

$$\bar{\kappa}_P = \bar{\kappa}_V + R/T \tag{5.52}$$

A proof of this relation is given in Example 5.7. Remember this holds for the ideal gas.

Temperature coefficients of energy and enthalpy. The product of an entropy capacitance and the temperature of the material is often used in place of the entropy capacitance. Here we have two such products:

---

[8] This is one of the reasons why Carnot's thermodynamics met with resistance. According to common prejudice, the heat capacitance of the ideal gas should be constant since "…facts have lately become known which support the view that heat […] consists in a motion of the least parts of bodies." (R. Clausius, 1850). On the mechanical theory of heat where heat is (a form of) energy, and assuming a kinetic theory, the heat capacity of the ideal gas turns out to be constant.

$$C_V = T\,K_V \tag{5.53}$$

$$C_P = T\,K_P \tag{5.54}$$

We will call the former the *temperature coefficient of energy* (just as in the case of pure heating discussed in Section 4.5.4), while the latter is the *temperature coefficient of enthalpy*. These names will be explained in Section 5.3. Traditionally they are called the *heat capacity (specific heat) at constant volume* and the *heat capacity (specific heat) at constant pressure*, respectively, since they are related to quantities of energy exchanged in heating at constant volume and at constant pressure.

Actual values of temperature coefficients. Since the entropy capacitances of the ideal gas are inversely proportional to the temperature of the body, its temperature coefficients must be constant. According to quantum theory, we would expect only two or three discrete values for the molar temperature coefficient of energy:

$$\bar{c}_V = \frac{1}{2} f R \quad , \quad f = 3, 5, 7 \tag{5.55}$$

The factor f is called the number of degrees of freedom. Monatomic gases have the value $f = 3$ at all temperatures, while many diatomic molecules exhibit $f = 5$ at room temperature; $f = 7$ is found for larger molecules. The gases found in nature agree with this rule to a modest extent (Fig. 5.14). The best agreement is found for the noble gases, which are monatomic molecules. Hydrogen gas displays the transition from $f = 3$ to $f = 5$ between 100 K and 400 K, after which a constant value of the temperature coefficient is maintained for several hundred Kelvin. Roughly speaking, this behavior is attributed to the "unfreezing" of internal modes of motion, rotation, and vibration, as the temperature increases.

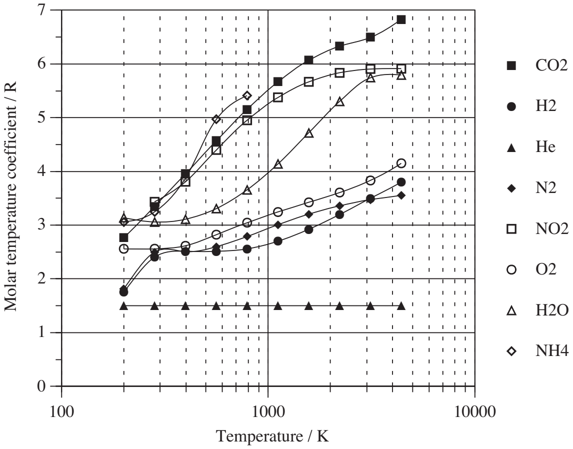


Figure 5.14: Values of the molar temperature coefficient of energy of various gases. Its value, divided by the gas constant, has been displayed as a function of temperature. The data have been computed using thermodynamic property functions implemented in the program EES (Klein et al. 1991).

5.2.9 A Dynamical Model of the Ideal Gas

Now we are ready to create a dynamical model of a body of (ideal) gas in a rather simple manner. As we have done in the previous sections, we start with the laws of balance of entropy and volume and add the constitutive laws, namely, the relation for the heating of the gas as in Equ.(5.22) and the equation of state (Equ.(5.25)). Naturally, we need the constitutive quantities of the gas as well, i.e., latent entropy (Equ.(5.37)) and entropy capacitance. The latter will be applied in the form of Equ.(5.50) with the adiabatic exponent as a parameter of the model. By rendering the relations in graphical form (Fig. 5.15) we might gain additional insight into the ideas that make up the model of the ideal gas. Once we have this model we can apply it to a couple of concrete cases such as Ruechardt's experiment for measuring the adiabatic exponent or the propagation of sound in a one-dimensional gas.

A basic model. To be concrete, let us consider a body of gas having a fixed amount of substance n with initial conditions for volume and temperature (there is a second form of the model where we prescribe temperature and pressure; this corresponds to the second form of heating in Equ.(5.27)). Heating/cooling and compression/expansion will be determined by the environment which means that the model should predict volume, entropy, temperature, and pressure as functions of time. The laws of balance of volume and entropy are simple—there is a production rate of volume, and heating is determined by a flux of entropy (Fig. 5.15). The remaining elements of the model are the expressions for the relation of volume and temperature with entropy and the equation of state. The former is applied in the differential form of Equ.(5.22) (yielding an expression for the rate of change of temperature which has to be integrated, see the center of the diagram in Fig. 5.15). The latter is used to calculate the pressure of the gas from volume and temperature.

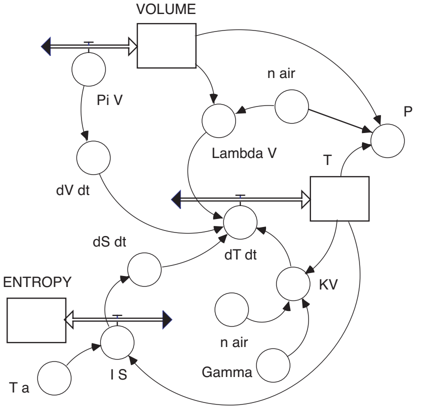


Figure 5.15: System dynamics diagram of the dynamics of an ideal gas. There are two laws of balance for entropy and for volume. Note that the structure that leads to the temperature of the gas is not a law of balance. It simply integrates the rate of change of temperature which follows from the constitutive law for the heating of the gas (Equ.(5.22)). The entropy current is calculated from the temperature difference and a conductance (not shown).

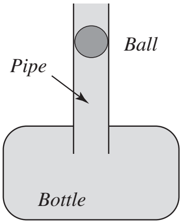


Figure 5.16: Ruechardt's experiment. A steel ball is dropped in a vertical glass pipe fitted to the top of a large bottle.

Rüchardt's experiment. There is a simple small experiment that allows us to measure the ratio of the entropy capacitances, i.e., the adiabatic exponent γ (Equ.(5.44)). A version of this experiment was already mentioned (Section 5.2.7 and Fig. 5.11). Here is an even simpler one. A large glass bottle is fitted with a long thin glass pipe sitting vertically at the top of the bottle (Fig. 5.16). If a steel ball is dropped into the pipe, it moves down and back up a few times before dissipation makes the oscillatory motion of the ball die down. The ball has to fit in the pipe very well so air does not escape and friction is not too great.

The model of this phenomenon consists of two parts, one for the body of air in the bottle (and in the pipe below the ball) and the other for the ball. The dynamical model for the air has already been constructed (Fig. 5.15). The part for the ball is standard for translational motion (Fig. 5.17, right). We formulate the law of balance of momentum of the ball. There are four momentum transfers affecting the motion: the one due to gravity, those resulting from the pressure of the air in the pipe above and below the ball, and finally the one due to friction. The momentum of the ball lets us calculate its speed. This concludes the second part of the model.

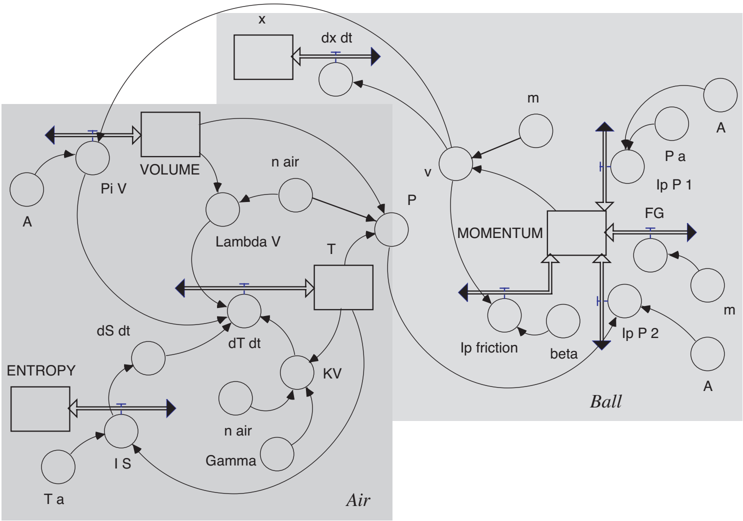


Figure 5.17: System dynamics model diagram for Ruechardt's experiment. Note the parts for the dynamics of the air (left) and the motion of the ball (right), and the two couplings (from speed to production rate of volume, and from pressure of the air to pressure force on the ball).

The interesting part of the combined model is the interaction of the motion of the ball with the dynamics of the air. As the ball moves down or up it compresses the air or lets it expand. In other words, its motion (its speed) determines the rate of production of volume of air by

$$\Pi_V = -Av \qquad \textbf{(5.56)}$$

where A is the cross section of the pipe and v denotes the speed of the ball (positive if it moves downward). The second interaction goes from the air to the ball: The changing pressure of the air in the bottle defines the variable force on the ball from below:

$$I_{p,P2} = -AP \qquad \textbf{(5.57)}$$

The complete model diagram is shown in Fig. 5.17. It shows how the model is composed of two distinct parts and how the elements interact. Simulation of the model and comparison of the results with data of the motion of the ball can be used to determine the adiabatic exponent of air (other parameters such as the volume of air in the bottle and initial temperature and pressure are measured directly in the experiment). The numerical result is 1.4 which agrees closely with other measurements and the expectation from Equ.(5.55).

If the motion of the gas is made adiabatic ($I_S = 0$ in Fig. 5.17, bottom left) and friction is turned off, the oscillation of the ball is an undamped harmonic motion since the amplitudes are small compared to the actual values of the variables (the volume of air in the bottle needs to be large compared to that in the pipe). The oscillatory period is directly coupled to the adiabatic exponent, so a calculation by hand can yield the desired result. What we do not find in this manner is the actual damped motion of the ball and the fact that entropy transfer affects this motion considerably. In fact, entropy transfer into and out of the air in the bottle leads to damping of the oscillatory motion—even without any friction present. This is a nice example of the effect of thermal dissipation (entropy production) in one part of the system that affects a totally different element of this system.

The propagation of sound in air. Another interesting application of the dynamics of a simple gas concerns the propagation of sound. Consider air at rest in a long cylindrical container with a source of sound at one end. Sound waves are longitudinal pressure waves (Section 3.6). Imagine two parcels (elements) of air (*Element* 1 and *Element* 2 in Fig. 5.18) moving back and forth as a consequence of the wave travelling through it. The motion of an element is modeled with the help of the balance of momentum (upper part of the system dynamics model diagram in Fig. 5.18). As the centers of mass of the elements move at different speeds, the air between them (*Element* 12) is compressed or expanded:

$$\Pi_V = A\left(v_2 - v_1\right) \tag{5.58}$$

In this manner, we can couple the motion of elements to the thermodynamics of the gas in intermediate elements.

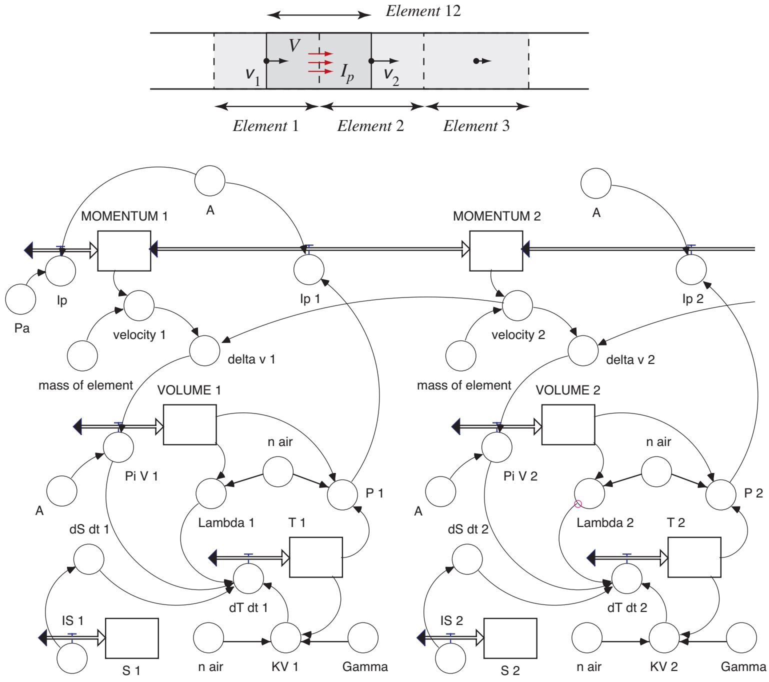


Figure 5.18: Diagram of a system dynamics model for a long line of gas divided into several elements. For each element, motion and thermodynamics are represented and coupled. Note the boundary condition for a pressure source at the left. We have to add a boundary condition at the right end of the line that corresponds to the concrete situation there (for example, a condition for the flow of momentum representing an open or closed end of a pipe).

The second part of the model represents the thermodynamics of an intermediate element (see Fig. 5.15). It couples back to the mechanical part of the model via its pressure which is equal to the momentum current density on the boundary between elements. If we divide the column of air into as many elements as is practical, we get a fairly useful representation of the dynamics of the complete system. Each element receives a model part as described and these parts are joined (Fig. 5.18). All we have to do to complete the model is to add proper boundary conditions at both end.

As speeds or pressures of subsequent elements are investigated during a simulation of the model, one can note shifts in peaks of the functions that tell us how long it takes for a disturbance to travel through a line of air. Correspondence with reality is fair—it depends to some degree upon the number of elements chosen to represent the physical system. If we assume the motion of the air to be adiabatic (zero entropy flow in the model), we get good results. Entropy transfer, on the other hand, leads to dissipation and damping of the waves, and to changes of the speed of sound.

5.2.10 Polytropic Processes

To conclude this section, let us consider a general kind of heating or cooling of which adiabatic or isothermal processes are special cases. Remember that in adiabatic processes, heat transfer vanishes while for isothermal changes, it takes a special value. In practice, it might take some intermediate value. For this reason, we write the current of entropy in the form

$$I_S = K\dot{T} \tag{5.59}$$

An operation conforming to this type of heating is called a *polytropic process*. K is a quantity resembling a generalized entropy capacitance. A number of practical processes may be modeled as polytropic changes, including a gas being compressed in a cylinder and being allowed to exchange entropy with the cylinder walls only, or the adiabatic convection of moist air. (In both these cases, the air is in contact with another material—container wall or water vapor—and by defining a polytropic process we can deal with the two components as a single system; see Example 5.8.)

This definition will now be applied to the ideal gas. Remember that this fluid can undergo only reversible processes. Now, with the rate of change of the entropy content expressed in terms of the entropy capacitance and the latent entropy, Equ.(5.22), and with the heating assumed for polytropic processes as in Equ.(5.59), we obtain the following equation of balance of entropy:

$$K_V\dot{T} + \Lambda_V\dot{V} = K\dot{T} \tag{5.60}$$

The latent entropy can be replaced by an expression involving both entropy capacitances (Equ.(5.31)) which leads to the differential equation for polytropic processes:

$$\frac{K_P - K_V}{K_V - K}\frac{\dot{V}}{V} + \frac{\dot{T}}{T} = 0 \tag{5.61}$$

We can recover adiabatic and isothermal processes if we set

$$\begin{aligned} K &= 0 && \text{for adiabatic processes} \\ K &= \pm\infty && \text{for isothermal processes} \end{aligned} \tag{5.62}$$

For the general polytropic process, K takes an intermediate value. If we introduce the *polytropic exponent*

$$\gamma^* = \frac{K_P - K}{K_V - K} \tag{5.63}$$

Equ.(5.61) becomes equivalent to the differential equation of adiabatic motion, which leads to the Poisson-Laplace law with γ replaced by γ^*. The polytropic exponent is a generalization of the adiabatic exponent. We shall always take it to be a constant, just as in the case of the ideal gas. The solution of Equ.(5.61) is a form of the law of polytropic processes of the ideal gas:

$$V^{\gamma^*-1}T = constant \tag{5.64}$$

which holds only if γ^* is a constant. Its form is equivalent to the laws of adiabatic motion of the ideal gas. Remember that it corresponds to a process in which the fluid is being heated in a particular way.

QUESTIONS

9. How does a gas respond to heat (entropy)?
10. What is the meaning of latent entropy in the case of a fluid not undergoing phase change?
11. What is the meaning of entropy capacitance at constant volume?
12. Air in our atmosphere is heated by the Sun. Is this process closer to heating at constant volume or at constant pressure?
13. What everyday observations can tell us that the entropy capacitance at constant pressure should be larger than the entropy capacitance at constant volume?
14. How do the curves for heating of the ideal gas at constant volume and at constant pressure compare in the *TS* diagram?
15. Why does a gas that is suddenly compressed get hot?
16. If air rises in the atmosphere, is the process isothermal or adiabatic?
17. A snugly fitting steel ball is dropped in a glass pipe that is sealed at the bottom. The air is compressed. Consider either isothermal or adiabatic compression of the air. In which case does the air get compressed more?
18. Bicycle pumps get hot when we quickly compress the air inside them. Does this mean the compression is not adiabatic?
19. In adiabatic processes, Equ.(5.39) tells us that the temperature of a body of gas should be at its maximum when the volume is smallest. Why? Why is this not true any longer if the gas is heated or cooled during compression or expansion?
20. Water between 0°C and 4°C shrinks when heated. What does this tell us about the latent entropy of water? What does this mean for the adiabats of water in the *TV* diagram?
21. Why is the difference between molar temperature coefficients of enthalpy and of energy equal to the gas constant?
22. On the basis of data in Fig. 5.14, what is the value of the temperature coefficients of energy and enthalpy of air at standard conditions? What does this mean for the expected value of the adiabatic exponent (ratio of the entropy capacitances) for air?
23. Why is the motion of the steel ball in Ruechardt's experiment (Fig. 5.16) damped if there is heat transfer between the air in the bottle and other bodies?
24. If moist air is compressed or expanded without heating or cooling, why is the process not adiabatic for the "dry" part of the air?

EXAMPLE 5.4. Change of the entropy content of the ideal gas.

Calculate the change of the entropy content of the ideal gas as a function of volume and temperature from the knowledge of the latent entropy and the entropy capacitance.

SOLUTION: According to Equ.(5.22), the rate of change of entropy of the gas is related to the rates of change of volume and temperature by the latent entropy and the entropy capacitance at constant volume. These are given by Equ.(5.37) and Equ.(5.53):

$$\begin{aligned}\Delta S &= \int_{t_i}^{t_f}\left[\Lambda_V \dot{V} + K_V \dot{T}\right]dt \\ &= \int_{V_i}^{V_f}\frac{nR}{V}dV + \int_{T_i}^{T_f}\frac{n\bar{c}_V}{T}dT\end{aligned}$$

Integration leads to

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) + n\bar{c}_V \ln\left(\frac{T_f}{T_i}\right)$$

The change of the entropy content does not depend on the initial values of volume and temperature, but rather on the ratio of their values at the beginning and the end.

EXAMPLE 5.5. The speed of sound in the ideal gas.

(a) Derive the formula for the speed of sound propagation in a fluid on the basis of the theory given in Chapter 3 (Section 3.6). (b) Use this result to derive the speed of sound in air for isothermal and adiabatic pressure waves, respectively. Measurements put the speed of sound in air at standard conditions at about 345 m/s. What does this mean for the type of process leading to the propagation of sound? Is it due to isothermal or adiabatic phenomena in air?

SOLUTION: (a) We have to compute the capacitance per length and the inductance per length of a fluid to compute the speed of sound according to Equ.(3.44) of Chapter 3. The capacitance per length is equal to the mass per length, which is

$$C' = \frac{\Delta m}{\Delta x} = A\rho$$

The inductance per length, on the other hand, may be calculated using Equ.(1.34) of Chapter 1. The momentum current density j_p is equal to the pressure P of the fluid. If there is a difference of speeds at the ends of a column of fluid of length Δx and cross section A, its volume is bound to change at a rate

$$\dot{V} = A\Delta v$$

According to Equ.(3.41), we obtain

$$\dot{V} = -L'\Delta x A^2 \dot{P}$$

which may be solved for the inductance per length:

$$L' = -\frac{1}{\Delta x A^2}\frac{dV}{dP}$$

The square of the speed of sound is equal to the inverse of the product *C'L'*. If we also change the derivative from volume to density we finally obtain

$$c^2 = dP/d\rho$$

for the square of the speed of propagation of sound in a simple fluid.

(b) The derivative of the pressure of the fluid with respect to its density has to be evaluated for the cases of adiabatic and isothermal compression. For the former we have the relation

$$P = \text{constant}\,\rho^{\gamma}$$

between pressure and density; see Equ.(5.47). The derivative is computed simply, and we obtain the final result

$$c_{adiabatic}^2 = \gamma\frac{P}{\rho} = \gamma\frac{R}{M_0}T$$

This expression is a result of the equation of state of the ideal gas, Equ.(5.26). Isothermal processes, on the other hand, lead to

$$c_{isothermal}^2 = \frac{P}{\rho} = \frac{R}{M_0}T$$

The numerical value for isothermal sound waves in air at 25°C turns out to be about 290 m/s (the molar mass of air is 0.029 kg/mole). This shows that sound waves travel about twenty percent faster than isothermal ones in air. The difference between the theory based on isothermal oscillations and actual measurements led Laplace to propose that sound waves are adiabatic. Data and theory lead to a value of the adiabatic exponent of air of 1.4.

EXAMPLE 5.6. The adiabatic temperature gradient in a gravitational field.

Air ascends and descends constantly in the Earth's atmosphere leading to a temperature gradient where temperature, pressure, and density of the gas satisfies adiabatic conditions. Show that in the Earth's atmosphere the *adiabatic temperature gradient* is constant. Compute its value for air, for which the ratio of entropy capacitances is 1.4.

SOLUTION: According to Equ.(5.48), the relation between pressure and temperature for adiabatic conditions is

$$P^{1-1/\gamma} = aT \quad , \quad a = P_0^{1-1/\gamma}\big/T_0$$

The temperature gradient *dT/dz* can be derived directly from this in terms of the pressure gradient *dP/dz*:

$$\frac{dT}{dz} = \left(1 - \frac{1}{\gamma}\right)\frac{T}{P}\frac{dP}{dz}$$

This gradient is commonly called the *adiabatic temperature gradient*. We can calculate the pressure gradient in the Earth's atmosphere according to the law of hydrostatic

$$\frac{dP}{dz} = -g\rho$$

where $g = 9.81$ N/kg is the gravitational field strength. If we replace the density, using the adiabatic relation

$$P^{1/\gamma} = b\rho \quad , \quad b = P_0^{1/\gamma}\big/\rho_0$$

we obtain for the gradient

$$\frac{dT}{dz} = -\left(1 - \frac{1}{\gamma}\right)\frac{g}{ab} = -\left(1 - \frac{1}{\gamma}\right)\frac{gM_0}{R}$$

which obviously is constant. The numerical value for air is

$$\frac{dT}{dz} = -\left(1 - \frac{1}{1.4}\right)\frac{9.81 \cdot 0.029}{8.31}\frac{\mathrm{K}}{\mathrm{m}} = -0.010\frac{\mathrm{K}}{\mathrm{m}}$$

This value is normally too large since humidity in the air changes the conditions. A correction can be made using the theory of polytropic processes (Section 5.2.10). A better value for the actual temperature gradient is – 0.006 K/m.

EXAMPLE 5.7. Temperature coefficient of enthalpy of the ideal gas.

(a) Express the molar entropy capacitance at constant pressure in terms of the entropy capacitance at constant volume. Transfer the result to the molar temperature coefficient of enthalpy. (b) Calculate the value of the temperature coefficient of enthalpy for a monatomic gas such as helium. Compare the result with measurements of the ratio of the entropy capacities, which is 1.66 for helium.

SOLUTION: (a) We use the relation between the entropy capacitances in the form of Equ.(5.31) and introduce the value of the latent entropy (Equ.(5.37)):

$$\begin{aligned} K_P &= \frac{nR}{P}\Lambda_V + K_V = \frac{nR}{P}\frac{nR}{V} + K_V \\ &= \frac{nR}{T} + K_V \end{aligned}$$

For the last step, the equation of state of the ideal gas was used. For molar quantities this yields:

$$\bar{\kappa}_P = \bar{\kappa}_V + R/T$$

The temperature coefficients are related to the capacitances by the temperature of the gas (Equ.(5.53) and Equ.(5.54)). Therefore:

$$\bar{c}_P = \bar{c}_V + R$$

(b) We obtain the numerical value of the temperature coefficient of energy for a gas whose molecules are single atoms from the expression in Equ.(5.55). With $f = 3$, the value is $3R/2 + \mathrm{R} = 5R/2 = 20.8$ J/(K·mole), which agrees closely with observation. With the ratio of the entropy capacitances measured, we determine the temperature coefficient of enthalpy (or of energy) according to Equ.(5.51). With the definition in Equ.(5.54) we have

$$\bar{c}_P = T\bar{\kappa}_P = \frac{\gamma R}{\gamma - 1} = 20.9\frac{\mathrm{J}}{\mathrm{K} \cdot \mathrm{mole}}$$

EXAMPLE 5.8. Polytropic compression of a body of ideal gas in a container.

Consider a certain amount of an ideal gas (body 1) which is enclosed in a cylinder having a piston (body 2). The cylinder and the gas are insulated from the environment; however, they may exchange entropy with each other. Derive the relation between the pressure and the volume of the gas if it is compressed. The temperatures of the gas and the cylinder walls are assumed to be equal during the process. The cylinder walls have an entropy capacitance K_2. (The associated temperature coefficient of energy is assumed to be constant.)

SOLUTION: We model both bodies as spatially uniform. Their heating takes the forms

$$\Lambda_{V1}\dot{V} + K_{V1}\dot{T} = I_{S1}$$
$$K_2\dot{T} = I_{S2}$$

Such bodies can undergo only reversible processes. Since their temperatures are equal at all times, the current of entropy leaving the gas is equal to the flux entering the walls. This leads to the following differential equation:

$$\Lambda_{V1}\dot{V} + K_{V1}\dot{T} = K_2\dot{T}$$

or

$$\frac{nR}{V}\dot{V} + \frac{C_{V1} - C_2}{T}\dot{T} = 0$$

Now we replace the rate of change of temperature by the rate of change of pressure, using the equation of state of the ideal gas. We obtain

$$\frac{nR + C_{V1} - C_2}{C_{V1} + C_2}\frac{\dot{V}}{V} + \frac{\dot{P}}{P} = 0$$

This is the differential equation of a polytropic process with the following polytropic exponent:

$$\gamma^* = \frac{nR + C_{V1} - C_2}{C_{V1} + C_2}$$

Without the temperature coefficient of energy of the walls, i.e., without the effect of exchange of entropy between the gas and the walls of the enclosure, the process would be adiabatic. Here, the polytropic exponent of the gas is smaller than its adiabatic counterpart.

5.3 THE ENERGY OF THE IDEAL GAS

In the previous sections we solved the constitutive problem of the ideal gas. In other words, we have the thermal equation of state of this fluid, and we determined its latent entropy and entropy capacitance. Now the energy of the ideal gas can be derived and the enthalpy—an energy related quantity—can be defined. When we consider energy transfers in heating we will finally understand the meaning of the temperature coefficients of energy and enthalpy. Our knowledge will then be applied to computing some cyclic processes undergone by the ideal gas.

5.3.1 The Energy and the Enthalpy of the Ideal Gas

Now that we have determined all the constitutive quantities of the ideal gas we should expect to be able to calculate other properties of this simple fluid. We have found the entropy of the ideal gas as a function of volume and temperature (Example 5.4). The energy function is just as interesting. How does the energy of the ideal gas depend upon the independent variables?

Also, other functions derived from the energy function are used to facilitate some computations. They are called *thermodynamic potentials*; among them are quantities such as enthalpy, free enthalpy, and free energy. In this section we will introduce the enthalpy of a fluid, and explain where the names *temperature coefficient of energy* or *temperature coefficient of enthalpy* come from.[9]

The Gibbs Fundamental Form of ideal fluids. We take the balance of energy in the form of Equ.(5.11) for granted. If we introduce the expressions for energy transfers, Equ.(5.12) and Equ.(5.13), and make use of the laws of balance of entropy and volume, we obtain

$$\dot{E} = T\, I_S - P\, \Pi_V$$

or

$$\dot{E} = T\, \dot{S} - P\dot{V} \qquad \textbf{(5.65)}$$

This is called the (dynamical expression of the) *Gibbs Fundamental Form* for a fluid that can undergo heating and compression. It is analogous to Equ.(4.35) for bodies that can undergo only heating and cooling. It relates quantities of the system only; there is no reference to processes (quantities exchanged) any longer. Here it has been derived on the basis of the theory of reversible processes of ideal fluids. It is interesting to note that this relation between system quantities (often called state variables) also applies to uniform irreversible processes as we shall see in Chapter 10.[10]

The energy function. Now we can prove an interesting and somewhat surprising result: *the energy of the ideal gas depends only on the temperature*. In other words, the values of the volume and pressure do not matter. As long as the temperature remains constant, the energy remains constant as well, and a change of the energy content of the gas depends only on a change of temperature. To prove this, let us start with the Gibbs fundamental relation for the ideal gas, Equ.(5.65). The rate of change of the entropy of the body is given by Equ.(5.22). Therefore,

$$\dot{E} = (T\Lambda_V - P)\dot{V} + (TK_V)\dot{T} \qquad \textbf{(5.66)}$$

Because of the form of the latent entropy in Equ.(5.37), the dependence of the energy upon volume vanishes. Therefore,

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[9] Thermodynamic potentials such as the enthalpy are basically unnecessary constructs that have arisen in traditional thermodynamics. The reason is simple: If we try to base the entire theory essentially upon energy, energy related quantities spring up and create an unwieldy formalism. Since we encounter these terms in traditional representations of thermodynamics we have to be aware of how to use them in some cases. I will restrict use of traditional terms to a minimum.

[10] Gibbs Fundamental Forms (GFFs) are traditionally assumed to be valid in different forms for different materials. Traditional thermodynamics—which basically is a theory of the statics of heat—is derived from these forms. They are commonly written as follows:

$$dE = TdS - PdV$$

so time has all but vanished from thermodynamics (Callen, 1985). In a dynamical theory of heat, however, GFFs are derived from laws of balance and constitutive relations for particular materials. This makes the theory much more flexible and has led to models for many more processes including those far from equilibrium (Müller, 1985; Jou et al., 1996).

$$\dot{E} = (TK_V)\dot{T} \tag{5.67}$$

or in integrated form,

$$E(T) = C_V(T - T_0) + E_0 \tag{5.68}$$

which holds since $C_V = TK_V$ is constant for the ideal gas. (Now we understand the term *temperature coefficient of energy* for C_V.) This result is important since it allows us to calculate processes undergone by the ideal gas in terms of a change of temperature only. We do not always have to follow the details of a process.

Enthalpy. The treatment of the constitutive problem of the ideal gas demonstrated the utility of the transformation of expressions to a form where pressure and temperature (rather than temperature and volume) are the independent variables. We can write the GFF in Equ.(5.65) with the help of Equ.(5.27) which yields:

$$\dot{E} = T\left(\Lambda_P\dot{P} + K_P\dot{T}\right) - P\dot{V} \tag{5.69}$$

If we add the term *VdP/dt* to this relation, we obtain

$$\begin{aligned}\dot{E} + P\dot{V} + V\dot{P} &= T\left(\Lambda_P\dot{P} + K_P\dot{T}\right) + V\dot{P}\\ &= \left(T\,\Lambda_P + V\right)\dot{P} + T\,K_P\dot{T}\\ &= \left(-T\frac{nR}{P} + V\right)\dot{P} + T\,K_P\dot{T} = \left(T\,K_P\right)\dot{T}\end{aligned}$$

The last line is a consequence of the equation of state of the ideal gas. If you introduce a new quantity defined as follows:

$$H = E + PV \tag{5.70}$$

you can see that

$$\dot{H} = \left(T\,K_P\right)\dot{T} = C_P\dot{T} \tag{5.71}$$

for the ideal gas. The quantity $H = E + PV$ is called the *enthalpy* of the fluid. We should not try to associate any graphical intuitive meaning with this term. Its utility becomes clear because of Equ.(5.71) for the ideal gas and relations commonly used in systems that exchange matter with their surroundings (Chapter 8). The term *temperature coefficient of enthalpy* for C_P is now obvious from Equ.(5.71).[11]

5.3.2 Energy Transfer in Heating

The foregoing allows us to calculate energy transfer due to heating and cooling at *con-*

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[11] Again, because of the identification of the energy transferred in heating with "heat" in traditional thermodynamics, the coefficients C_V and C_P have acquired the names *heat capacity at constant volume* and *heat capacity at constant pressure*, respectively, leading to considerable confusion as to the meaning of what is supposed to be a quantity of heat. Chemists often call the enthalpy the "heat content of a body."

stant volume or at *constant pressure*. In the former case we have

$$I_{E,th} = \dot{E} - I_{E,fluid} = \dot{E} = C_V \dot{T}$$

or

$$E_{th} = C_V \left(T_2 - T_1 \right) \tag{5.72}$$

This follows from the fact that, for constant volume, there is no energy exchanged as a consequence of compression or expansion. When we perform the same calculation for *constant pressure*, we find

$$I_{E,th} = \dot{E} - I_{E,comp} = \dot{E} + P\dot{V} = \dot{H} = C_P \dot{T}$$

or

$$\begin{aligned} E_{th} &= \Delta H \\ E_{th} &= C_P \left(T_2 - T_1 \right) \end{aligned} \tag{5.73}$$

If heating occurs at constant pressure, the energy added does not all stay in the system (remember the discussion of energy in phase changes, Section 5.1.2). So the energy *added* is not equal to the change of the energy of the body, rather it is equal to the change of its enthalpy.

Since for constant volume, $\Delta E = E_{th}$, Equ.(5.72) often leads learners to think that Equ.(5.68) holds only for processes at constant volume. Remember that Equ.(5.68) holds in general for the ideal gas, irrespective of the type of process undergone by the gas. Since the energy of the ideal gas depends upon the temperature only, its change is always calculated from the associated change of temperature.

5.3.3 Stirling and Otto Cycles

The thermodynamics of the ideal gas derives some of its significance from the fact that this gas can serve as a model fluid for practical power cycles. Put differently, the actual operations taking place in a variety of thermal engines may be modeled in terms of ideal gas processes. Since this fluid may undergo only reversible operations, the analysis of power cycles will deliver upper bounds for their performance. Here we shall discuss two important types of engines, the *Stirling* and the *Otto* engines. The former is an example of external combustion processes, while the latter uses internal combustion.

Stirling cycle. The Reverend R. Stirling invented an engine in which a gas such as air undergoes cyclic processes in a closed environment.[12] Two cylinders, a heater and a cooler, and a regenerator, make up the device. Burning of fuel for heating takes place externally and continuously, which in practice allows for much better control of the chemical process. This is important for pollution and noise control. Even though it is relatively difficult, and therefore expensive, to build, the Stirling engine has attracted renewed attention in recent years because of its inherent positive properties.

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[12] See for example G. Walker (1973 a,b) and J. Walker (1985).

It is convenient to discuss the operation of such an engine directly in terms of the model processes through which the ideal gas runs (Fig. 5.19). Let us begin with the heating of the fluid. The gas is heated, and expands at a constant temperature T_H. The entropy and the energy absorbed are simply related by this temperature. In the second step, the fluid is cooled at constant volume so that the temperature reaches its lower operating level, T_L. The entropy is discharged to the regenerator, a fact which will become important later in the cycle. Now the ideal fluid is cooled further at constant temperature, which means that its volume must be reduced; here the entropy is discarded through the cooler to the environment. In the final step, the gas is heated once again, this time at constant volume, to reach its initial temperature T_H. The entropy needed in this step is taken from the regenerator.

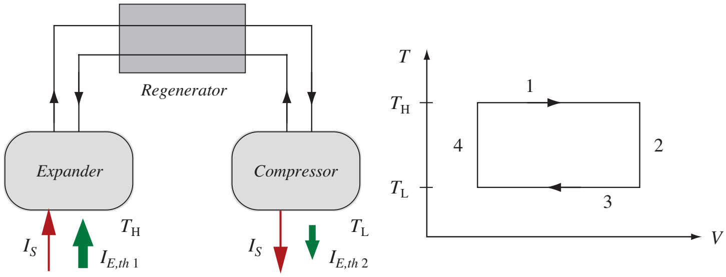

Figure 5.19: The Stirling engine consists of an expander, a compressor, and a regenerator. The fluid in the engine is expanded and heated at constant upper operating temperature T_H. The entropy emitted in the step 2 (constant volume cooling) is given back to the gas in step 4 with the help of a heat exchanger (the regenerator). Before that, the gas is compressed and cooled at constant lower operating temperature T_L. The ideal cycle is depicted in the *TV* diagram.

The regenerator's significance lies in increasing the thermal efficiency of the cycle. If we look only at the gas, two of the steps are the same as those in the Carnot engine. In the isochoric operations, however, additional entropy is exchanged between the environment and the fluid, thus reducing the efficiency of the engine compared to that of a Carnot cycle. If, however, the isochoric heating and cooling can be made internal to the system, we do not have to supply and waste extra entropy (and energy). In fact, a Stirling cycle having an ideal regenerator will achieve the Carnot efficiency. This is so because the same amount of entropy is emitted during the second step as is absorbed in the fourth (heating or cooling at constant volume between the same initial and final temperatures). If we include the regenerator in the system being considered, we have to model it as a body which always undergoes reversible operations at the same instantaneous temperature as the gas. In practice, the regenerator will be one of the weak links of the design: it will be difficult to minimize the production of entropy in this device. For modeling purposes we may consider it to be an ideal counter flow heat exchanger (Fig. 5.19).

Otto cycle. An example of an internal combustion engine is given by a fluid going through an *Otto cycle*. The gas is assumed to be air, and it is modeled as an ideal gas. In the first step the fluid is compressed adiabatically in a cylinder having a piston (Fig. 5.20). The temperature rises from its lowest value to the highest value achieved in the cycle. During step 2, the air is heated at constant volume as a consequence of the burning of fuel which has been mixed in with it. The final temperature is the highest in the complete cycle. Then the gas expands adiabatically, whereupon in a final step, it is cooled at constant volume.

The idealized cycle neglects several features which are a consequence of the internal combustion of the fuel. First of all, the production of entropy is modeled as taking place outside the fluid. We assume that the air absorbs the entropy released by the burning fuel as if it was isolated from it. The heating of the air is then assumed to proceed according to the laws laid down in this chapter. Also, in the real engine, air is taken up in each cycle, mixed with fuel, and expelled again from the cylinder with the products of the combustion. The air does not remain enclosed in the engine, and not just air runs through the steps of the Otto cycle. Rather, we have a mixture containing other components as well. In the model we neglect these facts. Still, the ideal Otto cycle is used as a first approximation of the real processes taking place.

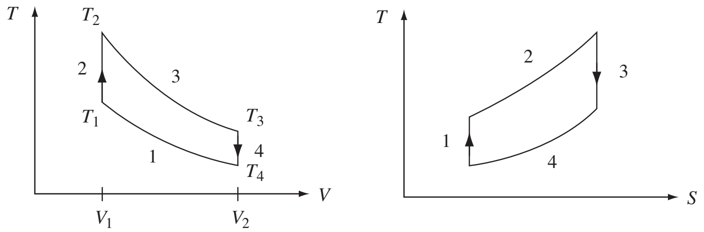

Figure 5.20: A body of ideal gas runs through an Otto cycle. The cycle has been drawn in the *TV* and in the *TS* diagrams.

5.3.4 Irreversible Processes, Constitutive Laws, and Time

Processes in nature are irreversible, but the theory laid down so far is one of reversible changes only. This is a direct consequence of the model of the ideal fluid I have chosen as a basis. The model is specified by the constitutive laws describing the body under investigation. Therefore the constitutive laws are responsible for the fact that the theory permits only reversible processes. As a consequence, a process undergone by a fluid can run at any speed with the same outcome—it is as if time did not really matter.

If we want to break out of the confinement of ideal processes, we have to change the model of the bodies undergoing thermodynamic processes. In other words, we have to enlarge the class of materials we are considering. The ideal gas defined by the thermal equation of state derived in Equ.(5.25) and the expression for heating as in Equ.(5.23), does not allow for anything but reversible changes. However, if we change the laws just a little bit we will find that thermodynamics is different.

An example of a simple body which is capable of irreversible changes is that of a viscous fluid (Chapter 10). Viscosity leads to the creation of entropy and to the dissipation of energy. We can introduce viscosity into our models by adding a viscous pressure term to the thermal equation of state of the fluid. This changes everything. Due to this term, the energy exchanged in the mechanical process does not reverse its sign upon reversal of the change of volume. As a consequence, the entropy exchanged will also be different for a process and its reverse. This is in stark contrast to the behavior of the ideal fluid we have investigated up to now. Fluids which behave in such a way produce entropy.

There is another consequence of changing the constitutive laws in the prescribed manner: time appears explicitly in the equations of change. Therefore, it matters how fast a process takes place. The equations describing a process will model real initial value problems as we know them from mechanics and other fields of physics. Only the particular properties of ideal fluids might make us believe that time has no place in thermodynamics. Time is right there; we only have to look for it.

QUESTIONS

25. A body of air is undergoing adiabatic change. Why does the model of fluids developed in this section tell us that the entropy of the body must stay constant?
26. What is the Gibbs Fundamental Form for isothermal processes of the ideal gas?
27. Why is the ratio of the temperature coefficients of enthalpy and energy equal to the ratio of the entropy capacitances at constant pressure and at constant volume?
28. The temperature of a body of air goes from T_1 to T_2 in adiabatic compression. By how much does the energy of the gas change? Why can we use the temperature coefficient of energy C_V to make this calculation?
29. A body of gas is heated at constant pressure. What happens to the energy absorbed by the gas as a consequence of heating? How much of it is stored in the body?
30. The enthalpy of a gas changes by – 10 kJ. How much energy has been transferred by heating/cooling at constant pressure?
31. Why is the ideal efficiency of the Otto cycle smaller than that of the Carnot cycle?

EXAMPLE 5.9. Isothermal heating of the ideal gas.

Determine the energy exchanged for the ideal gas in isothermal heating, i.e., calculate the energy supplied by heating and the energy exchanged as a consequence of volume changes. Use these results to show that the energy of the ideal gas should remain constant during an isothermal process.

SOLUTION: Since the temperature is constant during the process, the amount of energy exchanged in heating is obtained if we multiply the entropy absorbed by the temperature:

$$E_{th} = \int_{V_i}^{V_f} T\Lambda_V \, dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$$

The energy exchanged in the fluid process was already calculated in Equ.(5.32). Note that it is equal in magnitude to the expression just obtained, but it carries the opposite sign. Since the change of energy equals the sum of energies transferred, this change is equal to zero.

EXAMPLE 5.10. Measuring the temperature coefficient of enthalpy of air.

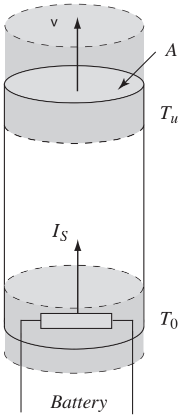

Figure Ex.10

Measuring the entropy capacitance at constant volume or the temperature coefficient of energy of gases is difficult since their values are small. For this reason, one often uses a flow method for measuring the corresponding values at constant pressure. Air is heated electrically at the bottom of a vertical open tube and flows upward (Fig. Ex.10). By measuring the speed of air flow and the temperature of the air at the top of the pipe we can infer the value of the temperature coefficient of enthalpy of the gas. (This is a simple experiment which can be built by hand.)

SOLUTION: Consider a certain amount of air which is heated at the lower end and then rises through the tube. We compare the two states of the body of air. If v is the speed of air leaving the tube, the amount of substance of the body of air flowing in time Δt is given by:

$$n = \frac{m}{M_0} = \frac{\rho(T_u) v \Delta t A}{M_0}$$

where A is the cross section of the tube, and T_u is the temperature of the air at the exit.

We can calculate the amount of energy transmitted to the air in a time Δt from the value of the power of the electrical heater. Since the process takes place at constant pressure, Equ.(5.73) tells us that

$$E_{th} = n\bar{c}_P\left(T_u - T_0\right)$$

If P_0 is the ambient pressure, the density of air at the outlet can be calculated using the equation of state of the ideal gas, Equ.(5.26):

$$\rho\left(T_u\right) = \frac{M_0 P_0}{RT_u}$$

Taken together, we arrive at the following expression for the molar temperature coefficient of enthalpy:

$$\bar{c}_P = \frac{RT_u}{AP_0\Delta T\, v}\frac{E_{th}}{\Delta t}$$

EXAMPLE 5.11. Energy exchanged in isochoric, isothermal, and adiabatic processes.

Compare the following operations: (1) an adiabatic doubling of the volume of one mole of air from standard conditions, and (2) isochoric cooling followed by isothermal heating which lead from the same initial to final states as (1). (a) Draw the processes in the *TV* diagram. (b) Calculate the energy exchanged as a consequence of mechanical and thermal processes for each step. (c) Determine the change of the energy content in (1) and (2), respectively.

SOLUTION: (a) The processes are shown in the *TV* diagram in Fig. Ex.11.

(b1) In the case of an adiabatic process undergone by an ideal gas with constant ratio of the entropy capacitances, we use the relationship between volume and pressure according to the adiabatic relations for the ideal gas:

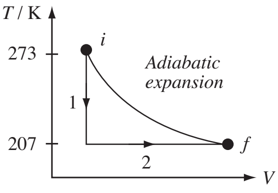

Figure Ex.11

$$PV^{\gamma} = P_i V_i^{\gamma}$$

If we solve this relation for the pressure, we can compute the energy exchanged as a consequence of compression or expansion:

$$E_{comp} = -\int_{V_i}^{V_f} P\,dV = -\int_{V_i}^{V_f} \frac{P_i V_i^{\gamma}}{V^{\gamma}}dV = \frac{P_i V_i^{\gamma}}{\gamma - 1}\left[\frac{1}{V_f^{\gamma-1}} - \frac{1}{V_i^{\gamma-1}}\right]$$

For standard conditions, the values of temperature and pressure are 0°C and 1 bar, respectively. The volume of one mole of an ideal gas at standard conditions turns out to be $22.4 \cdot 10^{-3}\ \text{m}^3$, and the ratio of the entropy capacities is 1.4 for air. Now the energy exchanged must equal

$$E_{comp} = \frac{1.013 \cdot 10^5 \cdot (22.4 \cdot 10^{-3})^{1.4}}{1.4 - 1}\left[\frac{1}{(44.8 \cdot 10^{-3})^{0.4}} - \frac{1}{(22.4 \cdot 10^{-3})^{0.4}}\right]\text{J} = -1.37\,\text{kJ}$$

The energy exchanged in the thermal process is zero for an adiabatic expansion: $E_{th} = 0$.

(b2) Let us number the isochoric and isothermal steps by 1 and 2, respectively. The energy exchanged in the fluid process is zero for the isochoric change:

$$E_{comp,1} = 0$$

For isothermal expansion or compression we have computed the energy exchanged in working in Equ.(5.32).The numerical value turns out to be

$$E_{comp,2} = -1 \cdot 8.31 \cdot 207 \cdot \ln(2)\mathrm{J} = -1.19\mathrm{kJ}$$

This is so since the temperature drops to 207 K in the adiabatic doubling of the volume (see Equ.(5.49)), and therefore also in the isochoric cooling. In the latter process the energy exchanged as a consequence of cooling is

$$E_{th,1} = \int_{T_i}^{T_f} C_V \, dT = C_V\left(T_f - T_i\right) = 1.0 \cdot \frac{5}{2} \cdot 8.31 \cdot (207 - 273)\mathrm{J} = -1.37\mathrm{kJ}$$

The temperature coefficient of energy has been computed according to Equ.(5.55), with $f = 5$.

The energy exchanged in isothermal heating is calculated using Equ.(5.23). Since the latent entropy of the ideal gas is *nR/V* (see Equ.(5.37) and below), we get

$$E_{th,2} = \int_{V_i}^{V_f} nRT/V \, dV = nRT \ln\left(\frac{V_f}{V_i}\right) = 1.0 \cdot 8.31 \cdot 207 \cdot \ln(2)\mathrm{J} = +1.19\mathrm{kJ}$$

(c) If we add up all the amounts of energy exchanged for the cases (1) and (2), we obtain the same value:

$$\Delta E = -1.37\mathrm{kJ}$$

This is as expected: the change of the energy content does not depend on the details of processes. Energy exchanged does depend upon the processes.

EXAMPLE 5.12. Thermal efficiency of the Otto cycle.

Consider a body of ideal gas going through the Otto cycle described in Fig. 5.20. (a) Determine the thermal efficiency of the cycle, and express it in terms of the temperatures involved. (b) Express the result in terms of the ratio of the volumes (compression ratio). (c) Compare the efficiency to that of a Carnot cycle.

SOLUTION: (a) The engine absorbs the same amount of entropy in step 2 as it emits in step 4. Since these steps involve heating and cooling at constant volume, the entropy exchanged is given by

$$S_{e,in} = C_V \ln\left(T_2/T_1\right)$$
$$S_{e,out} = -C_V \ln\left(T_4/T_3\right)$$

Therefore, we have the following relation between the temperatures involved:

$$\frac{T_2}{T_1} = \frac{T_3}{T_4}$$

The thermal efficiency may be expressed as the ratio of the energy delivered by working and the energy absorbed by heating. These quantities are given by

$$E_{th,in} = C_V\left(T_2 - T_1\right)$$

and

$$E_{comp} = C_V\left(T_2 - T_3\right) - C_V\left(T_1 - T_4\right)$$

The amounts of energy exchanged as a consequence of the mechanical operations in steps 2 and

4 are equal to zero. From this we conclude that

$$\eta_I = \frac{E_{comp}}{E_{th,\,in}} = 1 - \frac{T_3 - T_4}{T_2 - T_1} = 1 - \frac{T_4}{T_1}$$

(b) The temperatures and the volumes may be related by the adiabatic relations for the adiabatic steps 1 and 3:

$$T_2 V_1^{\gamma-1} = T_3 V_2^{\gamma-1}$$
$$T_1 V_1^{\gamma-1} = T_4 V_2^{\gamma-1}$$

which means that the thermal efficiency can be expressed as follows:

$$\eta_I = 1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

(c) The thermal efficiency of the Otto cycle is clearly smaller than the Carnot efficiency. The latter value would be obtained by an engine running between constant temperatures T_2 and T_4 (Fig. 5.20) which are the maximum and the minimum temperatures attained in the Otto cycle. The smaller efficiency is not due to dissipation (the engine is ideal) but simply due to the fact that entropy is absorbed at temperatures smaller than the largest one, and emitted at temperatures larger than the smallest one.

5.4 BLACK BODY RADIATION AS A SIMPLE FLUID

There exists another simple physical system of great interest in thermodynamics: thermal radiation which can permeate empty space and bodies alike. In its simplest form, the radiation field may be described from a thermodynamics viewpoint using very few variables. Radiation contains entropy. This becomes clear when we consider a body cooling down due to radiation only. Since entropy cannot vanish, the radiation must transport it away from the body. Radiation therefore constitutes a thermal system. In fact, thermal radiation trapped inside a cavity behaves just like a simple uniform fluid, very much comparable to the ideal gas. It is often called a *photon gas*. It possesses a certain amount of entropy and energy, and its pressure and temperature assume well-defined values.

The entropy and pressure of the radiation field turn out to be very small under everyday conditions on Earth, i.e., for small temperatures. For this reason, the properties of the radiation "fluid" are of interest mainly in astrophysics. It contributes considerably to the phenomena inside stars and in the universe as a whole. Transfer of entropy by radiation, however, may very well be appreciable even for low temperatures. Therefore, the radiation of heat plays a major role for engineers and scientists alike. In this section we shall study the photon gas; radiative transfer of heat will be discussed in Chapters 7 and 12 (see also Chapter 16 on solar radiation).

5.4.1 Thermal Radiation and Black Bodies

Bodies can emit and absorb electromagnetic radiation. If these processes occur because a body is warm or hot, we speak of *thermal radiation*. Radiation is a physical system in its own right, apart from the bodies which lead to its creation. A cavity, for example, may be filled with radiation which is continuously absorbed and emitted by the walls surrounding it (Fig. 5.21). We call the system inside the cavity the *radiation field* or the *photon gas*. Our task will be to decipher the thermal properties of this gas.

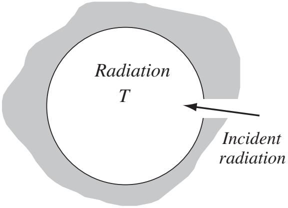

Figure 5.21: A cavity containing thermal radiation. The photon gas may interact either with the walls of the cavity or with a black body at temperature *T*, which is also the temperature of the photon gas. Radiation falling on a hole in the walls of the cavity will be completely absorbed. Therefore, the hole is said to act as a black body. Conversely, radiation emitted from it is called blackbody radiation.

The radiation inside the cavity may result from emission and absorption processes by the walls, which are kept at a temperature *T*. If the field is uniform, we can associate the same temperature with the radiation. The radiation filling the cavity is said to be *blackbody radiation*. We denote a body as *black* if it is an ideal absorber of radiation, i.e., if it absorbs all light rays falling upon it regardless of the frequency of the light. Consider a small opening in a wall of the cavity. Any light passing into the cavity from outside will have only a very small chance of ever escaping again. Therefore, we may think of the hole as an ideal absorber. Alternatively, light passing to the outside from the cavity must have the properties of radiation emitted by ideal absorbers—black bodies. In fact, the light emitted from a small hole in the walls of the cavity can be used to probe the properties of the radiation inside. (In Chapter 12 we shall investigate the relationship between the properties of the radiation field and the radiation flowing through space.)

We also may make the walls of the cavity completely reflecting in which case we need an ideally absorbing and radiating piece of matter, i.e., a black body, inside the cavity. The black walls or the black body serve as an entropy reservoir for the radiation field. Entropy is added to or removed from the field due to emission or absorption. If we do not wish to heat the photon gas, we can make do without any absorbing and radiating matter. In this case, we still can let the radiation undergo adiabatic processes.

5.4.2 Energy, Pressure, and Heating of Blackbody Radiation

As in the case of the ideal gas, we need to know some constitutive properties of the radiation field. From measurements on the radiation emanating from black bodies we can infer a relation between the temperature of radiation and the energy density of the photon gas. (The energy flux density and the energy density must be directly proportional; see Chapter 12) It is found that the intensity of light from the opening in the cavity in Fig. 5.21 does not depend on the nature of the walls, or on the size or the shape of the body emitting radiation. The temperature of the body, and therefore of the field, is the only parameter influencing blackbody radiation. Therefore, the energy density of the uniform field, i.e., the quantity

$$\rho_E = E/V \tag{5.74}$$

depends only on the temperature of the radiation enclosed in the cavity:

$$\rho_E = f(T) \tag{5.75}$$

Here, V is the volume of the photon gas, while E is its energy. $f(T)$ is an unknown function of the temperature.

Another important piece of information concerns the pressure of the photon gas. We know from electromagnetic theory that radiation transports momentum. While the pressure of radiation is very small under normal circumstances, it nevertheless can be determined experimentally. Both theory and experiment demonstrate that the pressure of the photon gas is equal to one third of its energy density:

$$P = \rho_E/3 \tag{5.76}$$

Since the energy density is a function of temperature only, the same is also true for the pressure. This is the *thermal equation of state* of radiation; it is comparable to the equation of state of the ideal gas. In the following subsections we shall exploit this information to derive further properties of blackbody radiation. But first we have to specify the heating of the photon gas.

We model blackbody thermal radiation as a spatially uniform system, which means that we associate with it single values of temperature and pressure. We will allow the volume of the cavity in Fig. 5.21 to be variable. Therefore, the independent variables used to describe the properties of radiation are volume and temperature, just as in the case of simple fluids. For this reason we can define the *latent entropy with respect to volume* and the *entropy capacitance at constant volume* of the photon gas; the procedure is analogous to the one used for the ideal gas in Section 5.2. More importantly, we shall assume that the uniform photon gas may undergo only reversible operations. Just as in the case of the ideal gas, the entropy depends upon volume and temperature with the latent entropy and the entropy capacitance as factors, and the heating is prescribed by Equ.(5.23).

Since the system can exchange energy only in thermal and fluid (mechanical) processes, just like any simple fluid, we obtain the same *Gibbs fundamental relation* as we do for the ideal gas, namely, Equ.(5.65). This is a direct consequence of the equations of balance of entropy and energy of the radiation field, and of the relationship between the heating and the rate of supply of energy, which is equivalent to Equ.(4.21).

5.4.3 The Constitutive Problem of the Photon Gas

We should now determine the latent entropy and the entropy capacitance of the photon gas, and with them the density of entropy and of energy. We can derive the missing information on the basis of the constitutive relations (5.75) and (5.76) if we consider a Carnot cycle undergone by the radiation inside a cavity. This is in accordance with the derivation carried out for the ideal gas in Section 5.2.6. Let the photon gas go through a Carnot cycle having very short adiabats, i.e., with a very small difference of the temperatures at which entropy is absorbed and emitted (Fig. 5.10). The energy released by an ideal Carnot heat engine is equal to

$$E_{th} = -\Delta T\, S_e \tag{5.77}$$

where S_e is the amount of entropy absorbed at the temperature of the furnace, $T + \Delta T$. On the other hand, the energy exchanged by the fluid during expansion can be computed easily from the pressure, which remains constant for the isothermal steps, and from the change of volume. The adiabatic steps do not contribute significantly to the exchange of energy since they are taken to be very small. For the same reason, the changes of volume are roughly the same for both isothermal operations (Fig. 5.10). If we also take into consideration that the pressure of the photon gas is equal to one-third of the energy density, and if we approximate the difference of pressures, we obtain

$$E_{mech} = -\left(P_{T+\Delta T} - P_T\right)\Delta V = -\frac{1}{3}\frac{d\rho_E}{dT}\Delta T\,\Delta V \tag{5.78}$$

The expressions in Equations (5.77) and (5.78) must be equal, which leads to a determination of the entropy added in one step of the Carnot cycle. This quantity is also equal to the integral of the latent entropy over volume. For this reason, the latent entropy with respect to volume of the photon gas must be equal to

$$\Lambda_V = \frac{1}{3}\frac{d\rho_E}{dT} \tag{5.79}$$

We introduce the rate of change of entropy into the Gibbs fundamental form—see Equ.(5.65)—and observe that the energy *E* is the product of the energy density and the volume. Since the energy density is a function of temperature only, its rate of change can depend only on the rate of change of *T*. All these considerations lead to the following result:

$$V\dot{\rho}_E + \dot{V}\rho_E = T\left(\Lambda_V\dot{V} + K_V\dot{T}\right) - P\dot{V} \tag{5.80}$$

or

$$\left(V\frac{d\rho_E}{dT} - TK_V\right)\dot{T} = \left(\frac{1}{3}T\frac{d\rho_E}{dT} - \frac{4}{3}\rho_E\right)\dot{V} \tag{5.81}$$

Since volume and temperature can be changed independently, each of the factors appearing in parentheses in Equ.(5.81) must be equal to zero. The right side leads to a differential equation for the energy density as a function of temperature which has the following solution:

$$\rho_E = aT^4 \tag{5.82}$$

or

$$E = aVT^4 \tag{5.83}$$

This is called the *law of Stefan and Boltzmann*; *a* is the *radiation constant*, and has a value of $7.56\cdot 10^{-16}$ J/(m$^3\cdot$K^4). It will be of crucial importance not only for deriving quantities related to the photon gas, but also when we calculate the energy associated with the radiation from hot bodies (Chapters 7 and 12).

We can now find the latent entropy and the entropy capacitance of the photon gas. The former quantity can be evaluated using Equ.(5.79). We obtain the latter if we set the factor multiplying *dT/dt* on the left-hand side of Equ.(5.81) equal to zero. The constitutive quantities turn out to be the following:

$$\Lambda_V = \frac{4}{3}aT^3 \tag{5.84}$$

$$K_V = 4aVT^2 \tag{5.85}$$

Finally, the rate of change of the entropy content of radiation can be expressed using the constitutive quantities. If we integrate the equation along a simple path in the *TV* diagram (Fig. 5.22), we obtain a simple result for the *entropy of blackbody radiation*:

$$S(T) = \frac{4}{3}aVT^3 \tag{5.86}$$

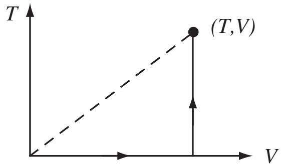

Figure 5.22: We integrate the expression for the rate of change of the entropy of radiation from the state $T = 0$, $V = 0$ to an arbitrary state. First, we integrate over *V* at $T = 0$, and then over *T* for a given value of *V*. The value of the entropy at $T = 0$ is set equal to zero.

This concludes the constitutive theory of the black body photon gas. The assumptions made are less accessible than in the case of the ideal gas; direct measurements of temperature or pressure are not that simple. Therefore, convincing ourselves of the validity of the results requires more indirect considerations such as those dealing with the transport of entropy and energy by radiation (see Chapters 7 and 12).

EXAMPLE 5.13. The ideal gas and radiation inside a star.

Both matter and radiation occupy the same region of space inside a star. If the temperature is high, the gas is completely ionized which makes it an ideal gas even at high densities. Because of the high temperature, radiation can contribute considerably to the pressure. (a) Matter inside a new main sequence star is composed of 70% hydrogen and 30% helium by mass. Calculate the total pressure of matter and radiation at the center of such a star of 15 solar masses, if the temperature and density have values of $34 \cdot 10^6$ K and $6.2 \cdot 10^3$ kg/m^3, respectively. Compute the fraction β of the total pressure which is due to the ideal gas. (b) Express the heating of the ideal gas plus radiation in terms of the gas pressure P_g and the radiation pressure P_r. (c) Calculate the expression for the total entropy capacitance in terms of the entropy capacitance of the ideal gas and the fraction β of the pressure due to the gas.

SOLUTION: (a) We can compute the gas pressure using the equation of state of the ideal gas in the form of Equ.(5.26). For this purpose we need the mean molar mass of the gas inside the star. Observe that for each mole of hydrogen nuclei we also have one mole of electrons, and for one mole of helium nuclei we also have two moles of electrons. This is a consequence of ionization. If we write X for the mass fraction of hydrogen, we have

$$M_0 = \left[\frac{2X}{M_{0H}} + \frac{3(1-X)}{M_{0He}}\right]^{-1}$$
$$= \left[\frac{2 \cdot 0.7}{0.0010\text{kg/mole}} + \frac{3 \cdot (1-0.7)}{0.0040\text{kg/mole}}\right]^{-1}$$

for the molar mass. The result is $0.615 \cdot 10^{-3}$ kg/mole. The pressures turn out to be

$$P_g = \frac{R}{M_0}\rho T = \frac{8.31 \cdot 6.2 \cdot 10^3 \cdot 34 \cdot 10^6}{0.615 \cdot 10^{-3}}\text{Pa} = 2.8 \cdot 10^{15}\,\text{Pa}$$

$$P_r = \frac{1}{3}aT^4 = 3.4 \cdot 10^{14}\,\text{Pa}$$

The ratio β of the gas pressure to total pressure is 0.89. In other words, 11% of the total pressure is due to radiation. There exist conditions in the universe under which radiation is responsible for an even larger fraction of the total pressure.

(b) We have to heat both matter and radiation simultaneously. Therefore, we simply add the expressions for the heating of both components:

$$I_S = \left(\Lambda_{Vg} + \Lambda_{Vr}\right)\dot{V} + \left(K_{Vg} + K_{Vr}\right)\dot{T}$$

This may be changed using the results obtained above

$$I_S = \left(\frac{nR}{V} + \frac{4}{3}aT^3\right)\dot{V} + \left(\frac{nR}{\gamma-1}\frac{1}{T} + 4aVT^2\right)\dot{T}$$
$$= \frac{1}{T}\left(P_g + 4P_r\right)\dot{V} + \frac{1}{T^2}V\left(\frac{1}{\gamma-1}P_g + 12P_r\right)\dot{T}$$

(c) The factor multiplying the rate of change of temperature in the foregoing equation is the total entropy capacitance of the mixture of ideal gas and radiation:

$$K_V = \frac{1}{T^2}V\left(\frac{1}{\gamma-1}P_g + 12P_r\right)$$

With $P = P_g + P_r$, $\beta P = P_g$, and $(1-\beta)P = P_r$, we obtain

$$\begin{aligned} K_V &= \frac{1}{T^2}V\left(\frac{1}{\gamma-1}\beta P + 12(1-\beta)P\right) \\ &= \frac{1}{T}\frac{PV}{T}\frac{1}{\gamma-1}\left[\beta + 12(\gamma-1)(1-\beta)\right] \\ &= \frac{K_{Vg}}{\beta}\left[\beta + 12(\gamma-1)(1-\beta)\right] \end{aligned}$$

For $\beta = 1$ the expression becomes the entropy capacitance of the gaseous component only.

5.5 THE COUPLING OF MAGNETIC AND THERMAL PROCESSES

With the exception of the brief description of melting and vaporization, this entire chapter has dealt with the coupling of thermal and mechanical processes in simple fluids only. The theory which has emerged may be called *thermomechanics*. It models only a small portion of what nature has to offer to us: basically all types of phenomena can be coupled.

Some magnetic systems exhibit a coupling of magnetic and thermal properties. In the simplest case, when such a body is heated its *temperature* can change, as well as its *magnetization* (Chapter 3). The properties of some paramagnetic substances have enabled physicists to reach very low temperatures in the laboratory by *adiabatic demagnetization* of the magnetic bodies. This is an interesting application, and it is worthwhile to extend thermodynamics to magnetocaloric effects. Since in previous sections we have carefully introduced a number of basic concepts, we can now present the material in a condensed form. You will find the motivation for the ideas developed here in the pages on the thermofluid processes of the ideal gas.

5.5.1 Equation of State of a Paramagnetic Substance

Paramagnetic substances exhibit simple coupling of thermal and magnetic properties similar to the coupling of fluid (mechanical) and thermal quantities which we have found in the case of the ideal gas or radiation. Remember that the thermal equation of state of the ideal gas expresses the relationship between the temperature, volume, and pressure of the fluid. In the case of a magnetic substance, the proper extensive and intensive quantities analogous to volume and pressure are the magnetization M and the magnetic field H, respectively (Chapter 2). It is found that the *thermal equation of state of a paramagnetic substance* can be written in the form

$$MT = C^{*}H \tag{5.87}$$

C^* is called the *Curie constant.* (Some values are listed in Table 5.3.) This law clearly shows the coupling between magnetic and thermal properties.

In the case of the ideal gas, knowledge of the constitutive law expressed by the thermal equation of state proved to be insufficient for a complete description of the system. We needed additional information, such as measurements of an entropy capacitance or of the ratio of the entropy capacitances, or knowledge of the form of the energy of the system. The energy of a system expressed in terms of the temperature and some other variable, is called the *caloric equation of state*. For paramagnetic substances it is found that the energy depends only on the temperature:[13]

$$E(T) = \frac{A}{1 + B\exp(D/T)} \tag{5.88}$$

where A, B, and D are constants. Remember that the energy of the ideal gas also is a function of temperature alone. It will be found that together with the laws of heating and the balance of energy we have enough information to model magnetocaloric processes of paramagnetic substances.

Table 5.3: Curie constant [a]

Paramagnetic Salt	M_0 / kg [b]	C^* / 10^{-5} m^{3}K · mole^{-1}
$Cr_2(SO_4)_3{\cdot}K_2SO_4{\cdot}24H_2O$	0.499	2.31
$Fe_2(SO_4)_3{\cdot}(NH_4)2SO_4{\cdot}24H_2O$	0.482	5.52
$Gd_2(SO_4)_3{\cdot}8H_2O$	0.373	9.80
$2Ce(NO_3)_3{\cdot}3Mg(NO_3)_2{\cdot}24H_2O$	0.765	0 [c]
		0.389[d]

a. Values taken from Zemansky and Dittman (1981), p. 473.
b. Mass of crystal containing N_A magnetic ions (N_A is Avogadro's constant).
c. Parallel component.
d. Perpendicular component.

5.5.2 The Heating of a Paramagnetic Substance

If a substance exhibits magnetocaloric coupling, its thermal and magnetic properties may change as a result of heating. Again, it is possible to have reversible processes, in which case we can write the constitutive law of heating in the following form:

$$I_S = \Lambda_M \dot{M} + K_M \dot{T} \tag{5.89}$$

The constitutive quantities have similar meanings as in the case of fluids. The factor multiplying the rate of change of the temperature must be a type of entropy capacitance. We call it the *entropy capacitance at constant magnetization*. The other factor is the *latent entropy with respect to magnetization*. You will see that the equations of state, together with the energy principle, allow us to determine these quantities. As in the case of fluids, we often use the quantity

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[13] Ionic paramagnetism and the production of low temperatures have been discussed in some detail in Zemansky and Dittman (1981), Chapter 18.

$$C_M = T K_M \tag{5.90}$$

which is called the *temperature coefficient of energy*. Also, in analogy to thermomechanics where we have used the pressure in place of the volume, it is practical to express the heating in terms of the intensive magnetic quantity, i.e., in terms of the magnetic field *H*:

$$I_S = \Lambda_H \dot{H} + K_H \dot{T} \tag{5.91}$$

Using the thermal equation of state, Equ.(5.87), we derive the following relationships between the different constitutive quantities:

$$\Lambda_H = \frac{C^*}{T} \Lambda_M \tag{5.92}$$

$$K_H = K_M - \frac{M}{T} \Lambda_M \tag{5.93}$$

5.5.3 Energy and the Gibbs Fundamental Form

The energy principle takes the following form for magnetocaloric processes. The energy of a body can change as a consequence of magnetic and thermal processes. Therefore the equation of balance of energy looks like

$$\dot{E} = I_{E,th} + I_{E,mag} \tag{5.94}$$

In Chapters 2 and 4 we found that the energy currents are given by

$$I_{E,th} = T I_S \tag{5.95}$$

$$I_{E,mag} = \mu_o H \dot{M} \tag{5.96}$$

If we plug these expressions into the equation of balance of energy, Equ.(5.95), and use the equation of balance of entropy for reversible processes,[14] we arrive at the *Gibbs fundamental form* which is analogous to Equ.(5.65):

$$\dot{E} = T \dot{S} + \mu_o H \dot{M} \tag{5.97}$$

This equation expresses the following observations: if the entropy of a body is increased at constant magnetization, its energy increases as well. Also, if the magnetization is increased at constant temperature, the energy grows. The GFF, Equ.(5.97), relates properties of the body only and does not refer to quantities which are exchanged in magnetocaloric processes.

The laws listed so far allow us to draw some important conclusions regarding the con-

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[14] The same reasoning that was applied to the ideal gas can be used here to the case of thermal and magnetic processes. See Section 5.2.1.

stitutive properties of paramagnetic substances. First, notice that the energy depends only on the temperature. Therefore the rate of change of the energy of a body is simply related to the rate of change of its temperature:

$$\dot{E} = C_M \dot{T} \tag{5.98}$$

If we introduce this into the Gibbs fundamental form, and observe that the rate of change of the entropy content is expressed by the entropy capacitance and the latent entropy, we get

$$C_M \dot{T} = T\Lambda_M \dot{M} + TK_M \dot{T} + \mu_o H \dot{M} \tag{5.99}$$

from which we conclude that the latent entropy with respect to magnetization is

$$\Lambda_M = -\mu_o \frac{H}{T} \tag{5.100}$$

This result is interesting. It tells us that if we lower the magnetization of a substance isothermally it *absorbs* entropy. According to Equations (5.98) and (5.88), we can calculate the entropy capacitance at constant magnetization. For temperatures which are not too low (in practice, this means some tenths of a Kelvin) the expression for the energy of the body given by Equ.(5.88) can be approximated. This leads to the following approximation to the entropy capacitance:[15]

$$K_M = \frac{A^*}{T^3} \tag{5.101}$$

where A^* has a constant value. With these properties derived we can calculate magnetocaloric processes and quantities.

5.5.4 Reaching Low Temperatures

Low temperatures can be obtained using liquid helium. However, this does not allow us to go lower than about 1 K. Today one uses paramagnetic substances to lower the temperature even further. This is done in the following manner: a paramagnetic substance whose temperature is near 1 K is slowly magnetized at constant temperature. Because

$$\dot{S} = \Lambda_H \dot{H} = -\frac{C^* \mu_o}{T^2} H \dot{H} \tag{5.102}$$

for *isothermal processes*, we notice that the body emits entropy during this step (Fig. 5.23). In a second step, the magnetization is reduced too quickly for entropy to be exchanged. Therefore this step is an adiabatic change (the vertical line in Fig. 5.23). According to Equ.(5.91), the mathematical law for this adiabatic process is

$$0 = \Lambda_H \dot{H} + K_H \dot{T} \tag{5.103}$$

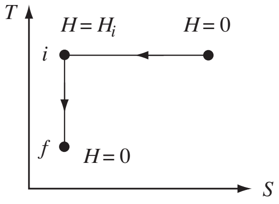

Figure 5.23: Lowering the temperature of a substance using adiabatic demagnetization. First, the field is increased isothermally at relatively high temperature. This leads to a reduction of the entropy in the body. Then the probe is demagnetized adiabatically, which leads to a decrease of the temperature.

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[15] Zemansky and Dittman (1981).

Since the latent entropy is negative, the temperature decreases with decreasing magnetic field. Thus we obtain lower temperatures as a consequence of *adiabatic demagnetization*.

EXAMPLE 5.14. Adiabatic demagnetization.

Determine the final temperature reached in adiabatic demagnetization in terms of the initial temperature and field. Compute the numerical value for the following example: chromium potassium alum has a Curie constant $C^* = 2.31 \cdot 10^{-5}\ \mathrm{m^3 \cdot K/mole}$ and an entropy capacitance constant $A^* = 0.15\ \mathrm{J \cdot K/mole}$. What temperature is reached if we start with values of 1.0 K and 2.0 A/m for the initial temperature and field, respectively?

SOLUTION: The effect is best determined on the basis of the expression for the heating given in Equ.(5.89), where we have to set $I_S = 0$. In addition, we need the latent entropy and the entropy capacitance as given in Equations (5.100) and (5.101), respectively. We arrive at the following differential equation of adiabatic demagnetization:

$$-\frac{\mu_o}{C^*} M \dot{M} + \frac{A^*}{T^3}\dot{T} = 0$$

If we change the temperature from T_i to T_f, and simultaneously change the magnetization from M_i to 0, the solution of this equation is

$$\frac{\mu_o}{C^*} M_i^2 = A^* \left(\frac{1}{T_f^2} - \frac{1}{T_i^2} \right)$$

We replace the magnetization by the field H according to the thermal equation of state to obtain

$$T_f = T_i \left[\frac{\mu_o C^*}{A^*} H_i^2 + 1 \right]^{-1/2}$$

The numerical value for this example is

$$T_f = 1.0 \left[\frac{4\pi \cdot 10^{-7} \cdot 2.31 \cdot 10^{-5}}{0.15} \left(2.0 \cdot 10^6 \right)^2 + 1 \right]^{-1/2} \mathrm{K} = 0.036\mathrm{K}$$

The values roughly correspond to those encountered in an experiment by De Haas and Wiersma in 1934.[16]

5.6 CHANGES OF STATE AND EQUILIBRIA

There are some common irreversible phenomena which we cannot describe based solely upon the simple theory of uniform reversible processes discussed in this chapter. Take, for example, the process encountered when two bodies of unequal temperatures are brought into thermal contact. We know that they eventually reach a state in which the temperature is uniform throughout. Simple measurements show that in the case of two identical bodies of water or metal at room temperature, the final tempera-

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[16] Quoted from Zemansky and Dittman (1981), p. 481.

ture is just the arithmetic mean of the initial hotnesses. A second example is the free expansion of air. Both phenomena lead to simple results. Still, the processes undergone by the bodies are clearly irreversible and cannot be dealt with on the basis of what we did in the current chapter.[17] However, there is another approach to thermal phenomena which will allow us to calculate such quantities as the final temperature reached in thermal contact, or the amount of entropy created in the free expansion of the ideal gas. Instead of calculating the details of actual irreversible processes using "equations of motion" we will compute only the *outcome* of such processes on the basis of a theory of the *statics of heat*. We shall do this only for some very simple cases. More details can be found in books on classical thermodynamics.[18]

5.6.1 Thermal Equilibrium

While the processes of the flow of heat in thermal contact, and of the free expansion of air, are more or less complicated, the initial and the final states are very simple and conform to the simplifying assumptions made in this chapter. At the beginning and at the end of the processes, the temperature, and possibly the density, are uniform throughout the systems. The state of uniform temperature is of particular interest.

Consider, for example, two blocks of metal which are placed in contact with each other. Assume that they are insulated from the surroundings by a wall which is impermeable to entropy. If the bodies have different temperatures initially, the hotter one will get cooler while the cooler body will get warmer. This continues until the temperatures have become equal. We interpret this process in terms of the transport of entropy from the hotter to the cooler body. The difference of temperatures is called the *thermal driving force*. Using the language introduced in the previous chapters, we say that a thermal driving force is needed to maintain the flow of heat from one body to another in thermal contact. Once the driving force has vanished, the process stops, and the temperature is uniform throughout the system. In analogy to mechanical or electrical situations in which the proper driving force is zero, we say that the system is in *thermal equilibrium*. Since equilibrium means the vanishing of the driving force between two systems, or between different parts of a system, thermal equilibrium means that the temperature must be uniform.

5.6.2 The Computation of Changes of State

We have dealt with the situation of uniform temperature before. In fact, we have built the theory of homogeneous processes upon the existence of such simple states. As before, we assume it to be possible to specify such states, which now are taken to be equilibrium states, by giving just one or two numbers, namely the temperature and the volume (in the case of systems whose volume may change). The theory of homogeneous processes laid down above has enabled us to calculate processes that carry bodies through states of uniform temperature and density, i.e., through states which are

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[17] We know from Chapter 4 how to model the example of uniform bodies in thermal contact by introducing resistive transfer elements. However, if we only have models of uniform reversible bodies at our disposal, even this simple example cannot be treated in a dynamical model.

[18] See H.B. Callen (1985) for an example of an approach to the statics of heat.

the same as those reached in equilibrium. The hope of calculating the results of irreversible processes now rests on the assumption that we have only to determine the changes from initial to final states irrespective of what happens in between:

> *In the absence of a proper theory of irreversible processes, we can still compute the outcome of such processes if they lead from one state of equilibrium to another. Under these circumstances we determine changes of state rather than the real processes.*

In other words, we assume that a theory of thermostatics of simple systems, which we have not yet developed, and which we are going to discuss only briefly, will lead to essentially the same relations as the theory of uniform reversible processes. There is a distinct difference, however, in what these theories are capable of delivering, and not just in their forms. The theory of reversible processes describes how states evolve. A theory of statics cannot do this. All it does is to deliver relations between the variables of systems in equilibrium. On the other hand, the number of materials which exhibit simple equilibrium states might be larger than the number of those which admit models of uniform processes.

Let us discuss the case of thermal contact of two rigid, homogeneous bodies. The total energy of the bodies is conserved since they are insulated from the surroundings:

$$\Delta E_1 + \Delta E_2 = 0 \tag{5.104}$$

According to the theory describing the heating or cooling of bodies at constant volume, the law of balance of energy leads to the following expression:

$$\int_{T_{i1}}^{T_f} C_1(T)\,dT + \int_{T_{i2}}^{T_f} C_2(T)\,dT = 0 \tag{5.105}$$

(see Equ.(4.40)). This is the proper equation for the *changes of state* of the bodies, rather than an equation describing the real processes undergone. The temperatures T_{i1} and T_{i2} are the initial temperatures of the two bodies, respectively, while T_f is equal to their common temperature at the end of the process. Graphically, this means that the areas under the curves C_1 and C_2 in the appropriate ranges must be equal. For the particular case where $C_1 = C_2$ for all temperatures, this rule is exhibited in Fig. 5.24.

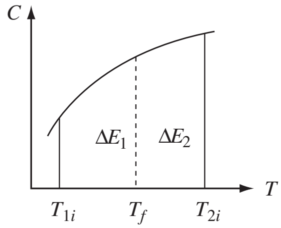

Figure 5.24: In the case of identical bodies, the final temperature reached in thermal contact is calculated simply by geometrical means. The energy emitted by the body which is cooling down is the opposite of the energy absorbed by the body being heated.

If we can calculate the integrals in Equ.(5.105), we can in principle solve the equation for the common temperature attained by the bodies in thermal contact. The simplest case is the one for $C = constant$. (See Example 5.15.)

Assume we have calculated the final temperature reached by the two bodies. We are now in a position to compute the *changes of the entropy content* of either one:

$$\Delta S_j = \int_{T_{ij}}^{T_f} \frac{C_j(T)}{T}\,dT \tag{5.106}$$

If we add the changes, we must get the amount of entropy produced:

$$S_{gen} = \Delta S_1 + \Delta S_2 \geq 0 \tag{5.107}$$

We expect the sum to be larger than zero. We will not give a general proof. Rather, the amount of entropy created is calculated for a particular case in Example 5.16.

5.6.3 Thermostatics and the Maximum Entropy Postulate

In mechanics, equilibrium states are dealt with in the branch called *statics*. *Thermostatics* is the science of heat which considers the determination of the equilibrium states. In this book we will not deal with statics. However, it is important to take a brief look at the theory.

In nature, equilibrium states can be the outcome of some processes. For example, a pendulum stops swinging after some time because of the effects of friction. Therefore, we could conceivably determine the equilibrium state of a pendulum by considering the mechanical processes which must be described, using proper constitutive laws. Naturally, these laws must include the phenomena which eventually make the pendulum stop swinging. Otherwise, our theory will never deliver the equilibrium states. Consider an ideal pendulum. No matter what we do, equilibrium simply cannot be attained if the body is moving at a given moment. This is the approach of dynamics. What we have attempted so far is to transfer the procedure known from mechanics to thermal physics. In this manner, thermodynamics is created.

There is a different approach to statics, however, an approach which has nothing to do with dynamics. It is best explained in the context of thermal phenomena. We shall use the example of bodies in thermal contact, which we have treated above. As you will see, the condition of equilibrium is determined by a new type of principle. The bodies start from equilibrium states and end in another state of uniform temperature. Initially, we assume the bodies to contain given amounts of entropy and energy, and their temperatures to be well defined. During the process, entropy is created. This finally stops when the temperature has become uniform throughout the combined system. In this final state, then, the amount of entropy contained in the system has attained its maximum possible value, which leads us to the *maximum entropy principle*:

> *The values assumed by the quantities specifying the equilibrium states of bodies are those which maximize the entropy of a body (or an assembly of bodies).*

When you think about it, this condition must also be satisfied in much more general cases than the one discussed. Entropy can be created, but it cannot be destroyed. Therefore, in a composite system which is insulated from its surrounding, the amount of entropy can only increase. In thermal equilibrium, the processes which are possible inside the system have come to a standstill and entropy is no longer produced. Therefore, the amount of entropy contained in the system has reached its maximum value.

The same kind of principle applies to other fields of physics as well. The determination of equilibrium states in mechanics can be built upon a similar variational principle. There is also a proper type of mathematics which deals with this kind of situation. For our purpose it is important just to recognize the difference between thermostatics based on the maximum entropy postulate, and thermodynamics, which follows from equations of balance and constitutive laws. In statics, equilibrium is determined without recourse to the equations of motion.

EXAMPLE 5.15. The final temperature reached in thermal contact.

Two bodies having *constant* values of $C = TK$ are brought into thermal contact. Assume that they are insulated from the environment. What is the final temperature reached?

SOLUTION: We simply use Equ.(5.105) in integrated form:

$$C_1\left(T_f - T_{i1}\right) = -C_2\left(T_f - T_{i2}\right)$$

where T_{i1} and T_{i2} are the initial temperatures of body 1 and 2. We obtain

$$T_f = \frac{C_1 T_{i1} + C_2 T_{i2}}{C_1 + C_2}$$

Note that this is only true if the values of C are constant. If the two bodies are identical or have identical values of C, we conclude that the temperature reached is exactly the arithmetic mean of the initial temperatures.

EXAMPLE 5.16. The entropy created in the contact of two bodies at different temperatures.

Two bodies having different temperatures T_{i1} and T_{i2} are brought into thermal contact; they are insulated from the surroundings. Their entropy capacities K are equal and are supposed to be inversely proportional to the temperature in the envisioned range; this means that the quantities $C = TK$ are constant. How much entropy is produced in the ensuing process of equalizing the temperatures?

SOLUTION: We can calculate the *changes* of the entropy content of the two bodies occurring as a consequence of the process. According to Equ.(5.106) we get

$$\begin{aligned} \Delta S &= \int_{T_{i1}}^{T_f} K\,dT + \int_{T_{i2}}^{T_f} K\,dT = \int_{T_{i1}}^{T_f} \frac{C}{T} dT + \int_{T_{i2}}^{T_f} \frac{C}{T} dT \\ &= C\left[\ln\left(\frac{T_f}{T_{i1}}\right) + \ln\left(\frac{T_f}{T_{i2}}\right)\right] = C\ln\left[\frac{T_f^2}{T_{i1}T_{i2}}\right] \end{aligned}$$

According to Example 5.15 the balance of energy leads to

$$\Delta E = C\left(T_f - T_{i1}\right) + C\left(T_f - T_{i2}\right) = 0$$

or

$$T_f = \frac{1}{2}\left(T_{i1} + T_{i2}\right)$$

We plug this into the expression for the change of entropy content to obtain $\Delta S \geq 0$. This is so because the arithmetic mean of the initial temperatures is always greater than or equal to their geometric mean. As a result, the argument of the natural logarithm in the expression for the change of the entropy content is larger than or equal to 1.

EXAMPLE 5.17. Production of entropy in the free expansion of the ideal gas.

Let a gas modeled as an ideal gas expand from a container into a second communicating one which is initially empty (this is called free expansion). The containers are assumed to be thermally insulated from the surroundings. Explain what is happening and calculate the change of entropy of the gas.

SOLUTION: The containers are isolated from their surroundings; therefore, the energy of the gas must remain constant during free expansion. Constant energy means constant temperature for an ideal gas. The result of free expansion is therefore the same as that of isothermal expansion. According to all we learned in this chapter, if an ideal gas expands isothermally, it absorbs entropy and the entropy content of the gas must increase. However, since in our example of free expansion entropy has not been exchanged, it must have been produced.

We interpret the process in the following manner. The energy used to produce entropy stems from the flow of the gas from points of high to points of low pressure. We say that the amount of energy which could have been used for other purposes has been dissipated.

In Equ.(5.36), we have calculated the amount of entropy communicated to a body of ideal gas undergoing isothermal expansion. Since the operation is reversible, the entropy exchanged and the change of the entropy content are equal:

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)$$

In free expansion exactly this amount of entropy must be generated internally, since the final states attained by the gas are the same irrespective of the details of the actual process. Therefore, in the free expansion of the ideal gas, the amount of entropy produced S_{prod} is equal to what has just been calculated

$$S_{prod} = nR\ln\left(\frac{V_f}{V_i}\right)$$

EXAMPLE 5.18. The final temperature reached in thermal contact: Maximizing the entropy.

Two identical rigid bodies with constant values of $C = TK$ are brought into thermal contact and insulated from the surroundings. Their initial temperatures are T_1 and T_2. Determine the final temperature assuming that the entropy of the bodies is maximized under the condition that the energy remains constant.

SOLUTION: The formulation of the problem tells us that we should try to find the maximum of the entropy of the system for given fixed energy. This is equivalent to the mathematical problem of finding the extremum of the function $S(E)$. Therefore, we need the entropy of the bodies as a function of their energies. According to Equ.(4.43), the energies are given by:

$$\begin{aligned} E_1 &= C\left(T_1 - T_0\right) + E_0 \\ E_2 &= C\left(T_2 - T_0\right) + E_0 \end{aligned} \tag{E1}$$

where

$$E = E_1 + E_2 = constant \tag{E2}$$

The entropy contents of the bodies have been calculated in Equ.(4.42):

$$\begin{aligned} S_1 &= C\ln\left(\frac{T_1}{T_0}\right) + S_0 \\ S_2 &= C\ln\left(\frac{T_2}{T_0}\right) + S_0 \end{aligned} \tag{E3}$$

We solve Equ.(1) for the two temperatures, replace E_2 using Equ.(2), and substitute the expressions into the equations for the entropies Equ.(3). If we add the two values of S we get:

$$S = S_1 + S_2 = C\ln\left[\left(\frac{E_1 - E_0}{CT_0} + 1\right)\left(\frac{E - E_1 - E_0}{CT_0} + 1\right)\right] + 2S_0$$

Now we look for the value of the energy E_1 for which the total entropy obtains its maximum. In other words, we have to set the derivative of S with respect to E_1 equal to zero:

$$\frac{\partial S(E,E_1)}{\partial E_1} = C\frac{1}{AB}\frac{1}{CT_0}\left[B-A\right]$$

with

$$A = \frac{E_1 - E_0}{CT_0} + 1$$

$$B = \frac{E - E_1 - E_0}{CT_0} + 1$$

This expression is equal to zero, which leads to the simple equation

$$E = 2E_1$$

This means that the entropy of both bodies is maximized if the energy of body 1 is half of the total energy. Naturally, body 2 must have half of the total energy as well. Inspection of Equ.(1) shows that the bodies have half of the total energy if their temperatures are equal to the arithmetic mean of the initial values:

$$T = \frac{1}{2}\left(T_1 + T_2\right)$$

This is the expected result. It shows that in the state attained by two bodies in thermal contact, but otherwise insulated from the surroundings, the entropy takes its maximum possible value.

EXERCISES AND PROBLEMS

1. (a) Demonstrate how the molar or specific entropy of fusion (or of vaporization) can be determined from a measurement of the energy flux of heating, the melting temperature (or the temperature of vaporization), and the rate of change of the amount of substance being melted (or vaporized). (b) A mixture of ice and water is heated by an immersion heater and stirred at the same time to insure homogeneous conditions. With an electric power of 50 W, 10 g of ice melt in 67.0 s. Calculate the specific entropy of fusion of ice.
2. Ice with a mass of 100 g (at a temperature of 0°C) is mixed with 300 g of water at 20°C inside a well insulated container. What will be the final temperature reached by the mixture? Will there be any ice left? How much entropy will have been produced?
3. Freon-12 is used in a refrigerator. It is evaporated at low temperature, thereby absorbing entropy from the space being cooled. Assume that freon is evaporating at –30°C. It will take up a current of entropy of 4.0 W/K. (a) At what rate does liquid freon convert to its gaseous form? The specific latent entropy of vaporization at –30°C is equal to 680 J/(K·kg). (b) What is the specific enthalpy of vaporization of Freon-12 at this temperature? (c) At what rate could ice be formed in the refrigerator?
4. Water is heated and then evaporated in an open glass standing upon a scale. Water temperature and mass are measured as a function of time (see diagram below, Fig. P.4). The immersion heater turns off at $t = 1600$ s. Data: Environmental temperature: 20°C, surface area of the wall of the container: $3.58 \cdot 10^{-2}$ m^2; entropy transfer coefficient through the wall (from water to the air): 0.039 W/K^{2}m^2; electrical power of the immersion heater: 304 W. In the following, consider the time t = 1400 s. (a) What is the immersion heater's rate of entropy production at this point? (b) What is the mass flow of the steam? (c) What is the flow of entropy through the walls of the container? (The bottom is well insulated.) (d) Determine the specific entropy of evaporation from the experimental data.

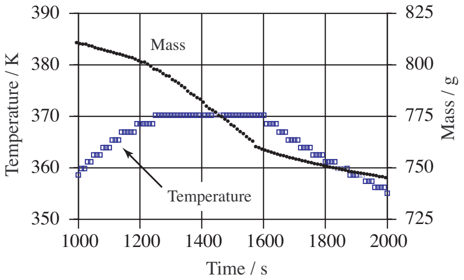

Figure P.4

5. A hot air balloon is floating at 2000 m above sea level in an atmosphere whose temperature is taken to be constant at all levels and equal to 0°C. The temperature of the air inside the balloon is 250°C. What is the radius of the spherical balloon, if it has a mass of 450 kg including the passengers? The pressure of the air at sea level is 1 bar.

6. A 10 cm long test tube is filled with air at a temperature of 27°C. The air is heated to a temperature of 57°C with the test tube open. Then it is placed upside-down in water so that a 5 cm length of the tube is above the water level (see the accompanying Fig. P.6). The air in the tube will cool down to 27°C. How far above or below the outer water level will the water rise in the test tube? Atmospheric pressure is set at 10^5 Pa.

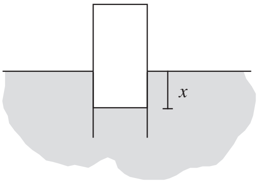

Figure P.6

7. Prove that the pressure gradient in the atmosphere of a planet is given by

$$P(h) = P_o \exp\left(-\frac{M_0 g}{RT} h\right)$$

if the temperature is held constant (isothermal atsmosphere). Hint: Remember Equ.(1.27), and use Equ.(5.26).

8. When a body of ideal gas expands or contracts, it exchanges energy as a consequence of the mechanical process. (a) Determine the energy exchanged for the ideal gas in an isothermal process for one mole whose volume is doubled. The temperature is 300 K. (b) How much entropy is exchanged?

9. A large bottle is fitted with a thin glass pipe (Fig. 5.16). If we drop a steel ball into the pipe it will oscillate there. (The diameter of the ball has to be slightly smaller than that of the pipe.) The oscillations are slow enough to be observed, yet fast enough to allow for the compressions and expansions of the air to be adiabatic. The bottle has to be large enough to leave the pressure and the volume of the air in it virtually unchanged. Derive the frequency of the oscillation.

10. In Example 5.6, the adiabatic temperature gradient in the Earth's atmosphere was computed for dry air. It was found to be – 0.010 K/m. More often, it is about – 0.006 K/m. The difference is due to the condensation of water vapor due to the decrease of temperature as the air rises. The process may be modeled more closely as polytropic heating of the gaseous component. The entropy comes from the change of phase of the other component. (a) Determine the polytropic exponent appropriate to this process. (b) Determine the coefficient *K* appearing in the expression of the heating of the gas. What is the significance of the sign of this quantity?

11. Stars are gas spheres which in most cases are nearly in hydrostatic equilibrium. Often, pressure and density are related by a law analogous to the one derived for polytropic changes. This might be due to convection (Chapter 14), or to a particular equation of state (degenerate gases). Derive the relationships between density and temperature, and between pressure and density, and the equation of hydrostatic equilibrium in a gravitating polytrope.

12. Express the energy exchanged in adiabatic expansion of the ideal gas in terms of the tem-

peratures. Remember that the energy of the ideal gas depends only on the temperature.

13. Use the Gibbs fundamental relation to derive the law of Poisson and Laplace, which holds for adiabatic processes of the ideal gas.

14. The following experiment can be used to measure the ratio of the entropy capacitances. The air in a large bottle is compressed to slightly above the external pressure, and the pressure inside is measured. Then we let air escape quickly through a valve so that the pressure inside is reduced to the external value. The temperature inside drops because this process is adiabatic. Finally, we heat the air slowly until it has the same temperature as at the beginning. The final pressure is measured. (This is called the method of Clément and Désormes.) (a) Draw a *TV* diagram of both steps. (b) Derive the ratio of the entropy capacitances from the values of the pressure. (c) Prove that the energy exchanged in the first step must be equal in magnitude to the energy exchanged during the second process.

15. A fluid whose energy content depends only on its temperature is expanded adiabatically; in a second step its temperature is brought back to its initial value at constant volume. It is found that in the adiabatic expansion the fluid exchanges an amount of energy equal to 50 kJ. (a) In what type of process is the energy exchanged during adiabatic expansion? What is the sign of the energy exchanged? (b) Is energy exchanged in the isochoric step? If so, in what types of processes, and how much? (c) Sketch the steps in a *TS* diagram (assume entropy to be conserved). Is it possible to visualize ΔE or amounts of energy exchanged in the diagram?

16. Exactly 1.0 g of water evaporates completely at 100°C and at a constant normal pressure of 1.0 bar to produce 1670 cm^3 of steam. Express the change of the energy of the water in terms of the changes of entropy and volume, and compute its numerical value.

17. How does the energy content change if water undergoes an isothermal expansion at a temperature of 2°C? Is the answer different for a temperature of 20°C?

18. A body of air with a mass of 20 kg at 100°C and 1.0 bar is compressed isothermally. (a) How much energy has to be supplied in the mechanical process if the volume is to be reduced to 10% of its initial value? (b) How large will the pressure of the air be at the end? (c) If the compression is to be performed at a constant rate of change of the volume in 10 s, how great does the mechanical power have to be as a function of time?

19. Determine the entropy content of one mole of argon at 300 K and at a pressure of 1 bar. (See the values supplied in Table 5.4.) The energy supplied in melting and in evaporating one mole of argon is 1.18 kJ and 6.52 kJ, respectively.

Table 5.4: Values of the molar temperature coefficient of enthalpy of argon[a]

Solid		Liquid		Gaseous	
T K	$\bar{c}_p$ $\mathrm{J \cdot mole^{-1}K^{-1}}$	T K	$\bar{c}_p$ $\mathrm{J \cdot mole^{-1}K^{-1}}$	T K	$\bar{c}_p$ $\mathrm{J \cdot mole^{-1}K^{-1}}$
20	11.76	83.85	42.04	87.29	20.79
40	22.09	87.29	42.05	100	20.79
60	26.59			300	20.79
80	32.13				
83.85	33.26				

[a] Values have been taken from Förstling und Kuhn (1983).

20. (a) What type of observation shows that the latent entropy (with respect to volume) of the ideal gas must be a positive quantity? (b) What must the sign of the latent entropy with respect to pressure be? What does the latter result mean? (c) Prove that the entropy capaci-

tance at constant pressure must be larger than the entropy capacitance at constant volume. What is the significance of this result?

21. Dry air rushes from the mountains (2500 m above sea level) into a valley (500 m above sea level). The temperature of the air in the mountains is 4°C. Before the arrival of the winds the temperature of the air in the valley is 16°C. By how much will the temperature of the air rise in the valley with the winds blowing?
22. Derive the expression for the pressure as a function of height in the Earth's atmosphere if pressure and volume are related by the adiabatic condition for dry air.
23. Why does the entropy content of the ideal gas remain constant as a result of an adiabatic process? Determine the special forms of the equations of balance of entropy and energy for such a process. What happens to the energy of the ideal gas during adiabatic expansion?
24. Derive the equations of adiabatic change of the ideal gas, using the result of Example 5.4, i.e., the equation which determines the change of the entropy of the ideal gas.
25. Measurements of the speed of sound in air at different temperatures give the following values. Determine the adiabatic exponent (the results are presented in the last column).

Table 5.5: The ratio of specific heats for 273.15°C and 101.3 kPa

Gas	c	M_0	γ
Argon	308	0.040	1.67
Helium	971	0.004	1.66
Xenon	170	0.131	1.67
Oxygen	315	0.032	1.40
Nitrogen	334	0.028	1.38
Carbon monoxide	337	0.028	1.40
Ammonia	415	0.018	1.29
Carbon dioxide	258	0.044	1.30
Methane	430	0.016	1.30

26. Draw the curve for an isobaric process of air in the *TS* diagram. Repeat the problem for the same body of air for a process at a higher value of the pressure.
27. A body of air is heated at constant pressure. What fraction of the entropy added remains in the body? What fraction of the energy added as a result of heating remains there?
28. Replace the process of heating of a body of air at constant pressure by two consecutive processes. The first is heating at constant volume, the latter is an isothermal change of volume. Sketch the steps in the *TS* diagram.
29. Consider a fixed amount of air in the atmosphere. Its momentary temperature is 15°C, the air pressure is 950 mbar. Now the sun radiates in such a way that in this fixed amount of air, energy is absorbed at a rate of 0.1 W. (a) At the beginning this fixed amount of air has a volume of 1.0 m^3. What is the amount of substance and the mass of the air? (b) At what rate does the entropy of this air increase at this moment? (c) What is the entropy capacitance at constant volume of the air in question? What is the entropy capacitance at constant pressure? (d) In the above mentioned process the pressure stays constant. At what rate does the temperature of the air change in the first moment?
30. Air having a mass of 5 g, at a pressure of 38 bar and a temperature of 650°C, is heated inside a cylinder by burning some injected fuel. The amount of energy added by the burning fuel is 7.5 kJ. The piston moves in such a way as to leave the pressure of the air constant. (This corresponds to a step in the Diesel process.) Assume that the fuel added does not change the properties of the air in the cylinder. (a) How much energy is exchanged as a result of the change of volume of the air? (b) Calculate the change of the energy of the gas.

31. A bubble of air with an initial diameter of 5.0 mm starts rising from the bottom of a pond at a depth of 5 m. The temperature of the water is 6°C at the bottom and 15°C at the surface. Assume the bubble to have the same temperature as the surrounding water at all times. Neglect the effects of surface tension. (a) Calculate the radius of the bubble shortly before it reaches the surface. (b) Estimate approximately the amount of energy exchanged as a consequence of heating while the bubble is rising.
32. Write the laws of balance of entropy and energy in differential and in integrated forms for (a) adiabatic processes of the ideal gas; (b) cooling of rigid bodies; (c) isobaric processes of the ideal gas; (d) isothermal processes of a fluid; (e) isothermal expansion of water at 2°C; (f) adiabatic processes of a fluid with internal production of entropy.
33. Use the law of hydrostatic equilibrium for a column of gas extending from the center of the Sun to its surface in order to estimate the pressure at the center. The gas at the center of the Sun is ideal. Determine the temperature at the center from a rough estimate of the density. How large is the contribution of radiation to the pressure at the center of the Sun?
34. The universe is permeated by blackbody radiation at a temperature of 2.7 K. This is commonly interpreted as a relic of a hot Big Bang. The expansion of space is described by a scaling factor *R* which increases with time. *R* is set equal to 1 at an arbitrary point in time. A simple model of the universe predicts that the temperature of the background radiation changes inversely with the scaling factor.[19] It is assumed that as the temperature of the universe dropped below a certain value, matter and radiation ceased to interact. (a) Show that as a consequence of this prediction, the expansion of the universe must be reversible. (b) The present mass density of matter in the universe is estimated to be $4.5 \cdot 10^{-27}$ kg/m^3. Determine the ratio of the mass densities associated with radiation and matter in the universe. (c) Express the dependence on *R* of the mass densities of matter and of radiation. At what value of *R* compared to today's value were both densities comparable?
35. The photon gas may undergo adiabatic and isothermal processes. (a) Express the relationship between temperature and volume for blackbody radiation for adiabatic processes. Show that blackbody radiation behaves as an ideal gas with a ratio of entropy capacitances equal to 4/3. (b) Determine the amounts of energy exchanged as a consequence of isothermal changes of volume, and compute the change of energy of the photon gas.
36. Consider the following strongly simplified model of a gas of noninteracting point particles. *N* particles are contained in a cube of side *L*. Assume one-third of the particles to travel in each of the three directions parallel to the sides of the cube. All particles have the same speed. (a) Show that the pressure of the particle gas is given by

$$P = \frac{1}{3}\frac{N}{V}v\,p$$

where v and p are the speed and the momentum of a single particle, respectively, and V is the volume of the cube. (b) Apply this result to an ideal gas of material particles. Derive the relation between the pressure and the energy density of the gas. (c) Again for the material ideal gas, derive the expression for the temperature coefficient of energy. Which gases have such a value for the coefficient? (d) Apply the idea to the photon gas. Show that the relation between pressure and energy density is given by Equ.(5.76).

37. In geophysics, the thermomechanical behavior of rocks in the Earth's interior is often described in terms of a fluid model. Which essential assumptions about properties of rocks have to be made for this model to apply?
38. Can you explain the difference between thermostatics and thermodynamics? Use Callen's definition of the task of thermostatics (which he calls thermodynamics) found in Footnote 3 of the Introduction for a starting point.

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[19] Peebles (1971), p. 121.

CHAPTER 6

TRANSFORMATION AND TRANSPORT OF SUBSTANCES

Processes that have to do with the nature and behavior of substances are called chemical processes. They deal with the quantity of chemical species, their strength or intensity relative to each other, and their power to cause other phenomena. Chemical processes are essentially of two types: Transport and reaction. Substances can wander from place to place, or they can change—in fact, they get produced or destroyed in chemical reactions. These are the phenomena we are going to introduce in this chapter. Bulk transport of fluids will be dealt with further in Chapter 8, and more formal treatments of chemical physics can be found in Chapters 10 and 15.

Much of the heat used for heating homes and power plants comes from the burning of fuels. Heat also strongly influences the chemical transformations upon which nature and many technical processes depend. Substances are stores for entropy and their reactions commonly produce entropy. These observations suggest that the study of chemical processes must be joined to an investigation of thermodynamics.

These facts should not mislead us into thinking that we can understand chemical phenomena only if we have studied thermodynamics. Traditionally, it is assumed in physical chemistry that one of the fundamental concepts we shall use here—the chemical potential—can only be derived from thermodynamic arguments and cannot be understood on its own account. This is simply not the case. We have the same intuitive feeling for this concept as we do for temperature in everyday life. Taking a direct road to the investigation of transformations of substances will make chemistry—and its relation to a theory of heat—so much more accessible.[1]

6.1 PHENOMENA AND MODELS OF CHEMICAL CHANGE

Chemical processes are those that deal with the quantity of substances, their strength or intensity relative to each other, and their power to cause other phenomena. We know this kind of thinking from our study of thermal, electrical or fluid phenomena in

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[1] The didactic concept behind the approach taken here owes much to the work of G. Job (1972). To my knowledge, G. Job was the first to suggest that an exposition of the subject of chemical change should start directly with the chemical potential as an easily grasped concept. See also Job (1983), Job and Herrmann (2006), Job and Rüffler (2011), D'Anna, Fuchs, and Lubini (2008), Fuchs (2009).

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_7,

the previous chapters—it is already clear what we are after, namely measures of quantity of chemicals, their intensity or the driving force of chemical transformations, and the power of chemical processes (i.e., the rate at which energy is released or used in chemical change). Here are some interesting phenomena that suggest how we can make sense of these concepts in chemistry. The discussion will be purely qualitative, leaving the quantitative treatment to the following sections.

Chemical reactions and amount of substances. It is customary to consider substances to be composed of the "building blocks" of matter, the elements. Consider some reactions involving elemental substances (simple substances) of the three elements hydrogen, oxygen, and chlorine (Fig. 6.1). If we start with a unit amount of hydrogen gas having a mass of 2 grams, we find that 16 g of oxygen gas will *completely* react with the hydrogen to form water. However, exactly twice that amount of oxygen gas, i.e., oxygen with a mass of 32 g, will react completely with 35.5 g of chlorine. Finally, twice as much chlorine, i.e., 71 g, will use up 2 g of hydrogen gas. Fig. 6.1 shows these examples written in the language of chemical reaction equations.

$$1H_2 + \frac{1}{2}O_2 \rightarrow 1H_2O$$

$$1O_2 + \frac{1}{2}Cl_2 \rightarrow 1ClO_2$$

$$1Cl_2 + 1H_2 \rightarrow 2HCl$$

Figure 6.1: Examples of chemical reactions written in the form of reaction equations. H, Cl, and O are the symbols for hydrogen, chlorine, and oxygen, respectively. Note the numbers (1, 2, 1/2) multiplying the symbols of the substances (H_2, O_2, H_2O…); these are the stoichiometric coefficients.

Interpretation. We see that the mass of a certain quantity of an elemental substance cannot serve as a natural measure of amount of substance. It appears that 71 g of chlorine are chemically equivalent to 2 g of hydrogen. Therefore, it is necessary to introduce a new measure of *amount of substance*. If we count 2 g of hydrogen gas as one unit of amount of substance, called 1 mole, the reactions tell us that 1 mole of hydrogen gas (H_2) has a mass of 2 g, 1 mole of oxygen gas (O_2) has a mass of 32 g, while the mass of 1 mole of chlorine (Cl_2) is 71 g. The mass of one mole of amount of substance is called the *molar mass* of the substance.

According to the particle model of the structure of substances, equal amounts of substance correspond to equal numbers of particles (1 mole corresponds to $6.02 \cdot 10^{23}$ particles). This gives us additional insight into how to understand the nature of quantity in processes having to do with substances. Hydrogen gas H_2 and chlorine Cl_2 form hydrogen chloride HCl. If we use one mole of H_2, we have two moles of H-atoms; the same applies to Cl_2. Now, two moles of H-atoms and two moles of Cl-atoms form two moles of HCl molecules.

Pressure of dilute gases and the measure of amount of substance. Substances can be brought into gaseous form. If the gas is dilute or hot enough, or both, all substances show the same behavior (*ideal gas*; see Chapter 5 for more details). If we fill such a gas into a container of given volume at a prescribed temperature, the following can be observed. It takes different masses of the gas for different substances to obtain the same pressure. For example, 2 g of hydrogen gas, 71 g of chlorine, or 32 g of oxygen gas all have the same pressure if volume and temperature are the same.

Interpretation. According to what we know from reactions, 2 g of hydrogen gas, 71 g of chlorine, or 32 g of oxygen are equal amounts of the three substances (H_2, Cl_2, and O_2, respectively). Therefore, the pressure of simple gases depends upon the amount of substance of the gas, not upon its mass or some other possible measure. In the particle model, it takes equal numbers of particles to get the same pressure for the same volume and temperature.

Distribution of toluene in water and air. One of the best known facts about substances is that they spread through materials and space. If you spill a bad smelling substance in a room, eventually bad odor will evenly fill the room. In a homogeneous environment, i.e., an environment that is the same everywhere, a substance diffuses and distributes evenly if we wait long enough.

This is not the case if the substance can travel through and spread in different materials in contact with each other, such as water, air, and soil. For example, toluene diffuses from water into air until the concentration of toluene is about four times higher in water than in air (Fig. 6.2). We see the concentration in water starting at a high value; there is no toluene in the air. As the concentration decreases in water, it increases in air. After a little more than half an hour, the concentrations have reached what we call equilibrium values. They do not change any longer.

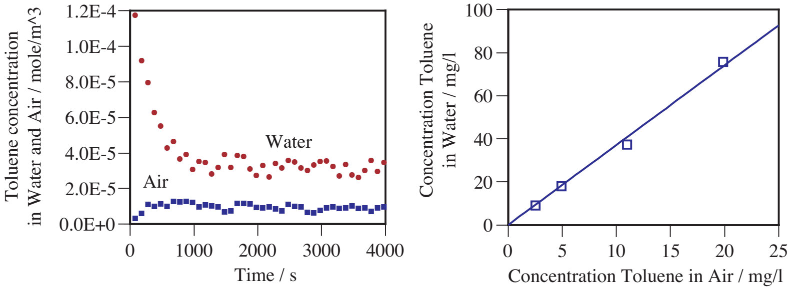

Figure 6.2: Toluene spreads in water, air, and soil. Dynamic case (left: concentrations of toluene in water and air; data for soil not shown). Equilibrium relation between concentrations of toluene in air and water, (right). Data courtesy J. Hosang.

Interpretation. The spreading of a dissolved substance in a homogenous background is credited to differences in concentration. Quite obviously, substances diffuse from areas where they are more concentrated to places where the concentration is lower. When the concentration of a substance has become uniform, when there is no concentration gradient left, the substance does not flow any longer.

This explanation does not work with a substance spreading through different environments in contact with each other. It appears that toluene “prefers” to be in water rather than in air. So, if there are equal concentrations of toluene in water and air in contact, there still is a tendency of toluene to migrate into water; it is as if there were a chemical tension between toluene in water and in air. We can explain this by introducing the concept of *chemical driving force* and *chemical potential*. At equal concentrations, the chemical potential of toluene is lower in water than in air. The chemical potential is conceptualized as a the innate tendency of a substance to change (to migrate somewhere else or to decay). The difference of the chemical potentials of toluene in water and in air is interpreted as the *driving force* for the flow of toluene from one environment into the other. The observation tells us that the driving force for the flow of toluene cannot be differences in its concentration; rather, it must be the gradient of the chemical potential of a substance (Fig. 6.2).

Note the shape of the concentration of toluene in water which resembles data we have seen in discharging of containers and capacitors. This suggests that the chemical process of diffusion depends upon the chemical potential difference in a manner similar to how currents of water and charge depend upon pressure differences and voltages.

Is the difference in concentration or in chemical potential the cause for a flow of a substance? The question is analogous to whether level or pressure differences are the driving forces for flows of liquids between communicating tanks (Section 1.1 of Chapter 1). If we fill oil in one tank, water in the other, we have differences of densities, levels, and pressures so which is the most general concept that explains the phenomena? Clearly, both densities and levels matter, but in the end, pressure differences always explain what is happening—it is the proper potential for fluid flow.

Transformation of glucose. Glucose (D-glucose, dextrose, simple sugar) exists in two different configurations (called anomers) that only differ in the spatial arrangement of the atoms in its molecules (the elemental composition and therefore the molar mass is the same). The configurations are called α-glucose and β-glucose, respectively. Originally, pure α-glucose is dissolved in water. Slowly, part of it will change into β-glucose (Fig. 6.3). (The anomers are optically active and rotate the plane of polarized light passing through a solution. Since the effect is different for α-glucose and β-glucose, a change in composition leads to a change of angle of rotation which can be measured.)

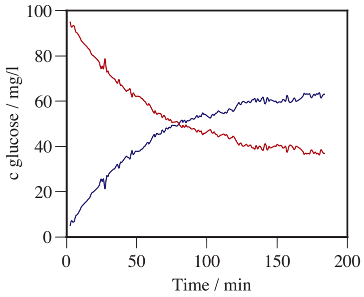

Figure 6.3: Concentrations of α-glucose (decreasing curve) and β-glucose in water as functions of time. α-glucose decays into β-glucose (the phenomenon is called mutarotation of glucose). The concentration is determined by measuring the rotation of the plane of polarization of plane-polarized light shining through a solution of glucose. Data courtesy B. Sonnleitner.

Interpretation. Both configurations of glucose have a tendency or drive to change. The strength of this tendency can be expressed in terms of the chemical potential, just as we did in the case of the tendency of a substance to disperse. α-glucose and β-glucose have different standard chemical potentials (when the concentration takes a standard value), and these potentials also depend upon concentration. If there is a difference in chemical potential, there is a driving force for change (for a reaction). Once the chemical potentials have become equal, this chemical driving force becomes zero and the reaction stops. The experiment shows that the chemical potentials of α-glucose and β-glucose become equal at different concentrations. This behavior is the same as that observed for the tendency to disperse (see Fig. 6.2).

The dynamics of the reaction is again similar to many other processes we have observed: Charging and discharging of containers and capacitors, slowing down of a spinning wheel, cooling and heating of bodies at different temperatures, diffusion of toluene (Fig. 6.2), etc. The chemical potential difference seems to take a similar role to differences of pressure, temperature, electric potential, and angular speed.

Soaking potato cores in water. Spherical potato cores of roughly the same size are soaked in distilled water, and in water with some dissolved table salt. In the course of time, the mass of the potato cores changes (Fig. 6.4). If there is only water, or water with a low concentration of salt, the cores grow. If the salt concentration is above a certain value, the cores lose mass. At a certain concentration (called isotonic), the mass does not change. If sugar is used instead of salt, it is found that it is isotonic if the molality (concentration measured as amount of substance per kilogram of solvent) is about twice that of salt.

Interpretation. Since the mass of the cores changes, substances must be flowing into or out of the cores. We have already seen that substances such as salt can diffuse through materials. However, this case is different. Take the example with pure water (0% salt in Fig. 6.4). The core is taking up substance, but the only substance present outside is water. Therefore, water is flowing into the potato. Even if a little salt is present in the solution, the potato takes up water. If the concentration of salt is larger than a certain critical value, the potato core loses water. (This last point is not so clear; we would have to prove more carefully that there are no other substances—such as minerals—being washed out of the core.)

Usually we say that water flows from points of high pressure to points of low pressure. Take the case of a core in pure water. If we adhere to this interpretation, we must conclude that the pressure of the water inside the potato core is lower than the pressure outside. The core consists mostly of water with different substances dissolved in it. This indicates that the pressure of water is lower when substances are dissolved in it.

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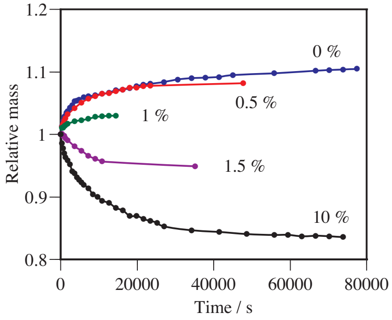

Figure 6.4: Relative mass of potato cores as a function of time. The cores are placed in distilled water containing different concentrations (percent by mass) of table salt. If placed in pure water, the cores grow. If more salt is dissolved, the cores grow less and less. They lose mass if the concentration of salt increases beyond a critical value.

If we accept this conclusion, we can explain the other observations as well. If salt is introduced in the water outside, its pressure decreases. Therefore, the pressure difference of the water outside and inside the core becomes smaller, letting less water migrate into the potato. Finally, at a certain concentration, the water pressure inside and outside is equal. With still more salt dissolved outside, water will actually flow from the core into the solution surrounding it.

This transport of water is called *osmosis*. Osmosis is water transport across selectively permeable membranes (such as the potato cell walls) between different aqueous solutions. Pressure is an indication of the chemical potential of a liquid. Solutes (dissolved substances) decrease the pressure and therefore the chemical potential of water. If the concentration of amount of substance of solutes is higher in a batch of water, and lower in another, water flows from where there is less solute to where there is more.

Observing that isotonic solutions of salt or sugar are obtained if the molar concentration is the same (except for a factor of 2)—and not if the concentration by mass is made equal—again shows that amount of substance counts, not mass. In fact, the factor 2 is the result of the dissociation of table salt into Na^+ and Cl^- ions, making twice as many particles per mole as in the case of sugar.

Blood cells in a solution. Red blood cells are placed into an isotonic aqueous solution. Nothing should happen—there should not be any flow of substances across the cell walls. If we now introduce a solute that can cross the cell membranes in the bath, the cells shrink rapidly at first by about 10%. Then they slowly regain their original volumes (Fig. 6.5).

Interpretation. The added solute raises the concentration of dissolved substances in the bath relative to the inside of the cells. Two things happen: Water will flow out of the cell into the bath (osmosis), and solute will travel into the cell (diffusion). Since only the amount of water in a cell effectively determines its volume, the volume of the cells decreases at first (Fig. 6.5).

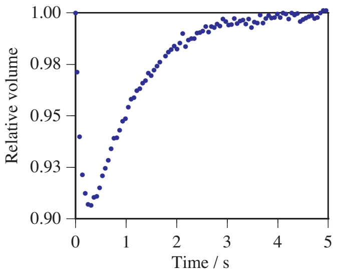

Figure 6.5: Red blood cells first shrink when a solute is introduced in an isotonic watery solution. Then they slowly regain their original size. Data from Macey and Oster (UC Berkeley).

At a certain point, the flow of water stops (the chemical potentials of water inside and outside have become equal). However, the permeable solute continues to diffuse (it only reacts to gradients of its chemical potential which depend upon its own concentration gradients). Since the concentration of solutes continues to grow inside the cells, the pressure of the water inside decreases and water changes its direction of flow. The cells grow (Fig. 6.5).

Burning of fuels. Fuels such as hydrogen, methane, carbon, or gasoline are allowed to burn when reacting with oxygen. We burn fuels to produce entropy for heating homes or engines. It is observed that different fuels produce different amounts of entropy per mole of fuel.

Interpretation. Clearly, burning fuels produces entropy. We know from our discussion of thermal processes that we need a process that releases energy to cause entropy to be produced. Therefore, the reaction of a fuel such as hydrogen with oxygen must release energy. The quantity of energy released certainly depends upon the quantity of fuel burned. If different substances yield different amounts of entropy, there must be different chemical driving forces in these different reactions: some fuels are "stronger" than others.

Batteries and fuel cells. Batteries and fuel cells are devices that allow us to use voluntary chemical reactions to set up a voltage and drive an electric current. The open circuit voltage of electrochemical cells are between about 1 and 4 Volts.

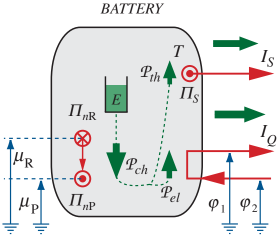

Figure 6.6: Process diagram of a battery. Chemical reactions release energy which is used to pump electric charge. In a real battery, some of the energy released leads to the production of entropy. (R: reactants, P: products.)

Interpretation. Chemical processes can cause other processes. Put differently, voluntary chemical reactions *release energy* (Fig. 6.6; there is a sink of the chemicals being consumed, and a source of the chemicals being produced; the total effect is the transition of chemicals from higher to lower chemical potential). In electrochemical cells, the energy is used to pump electric charge (in reality, a part of the energy released is always used for entropy production: processes are not ideal). The power of the electric process depends upon the electric current and the voltage set up. Analogously, the power of the chemical process depends upon the chemical driving force of the reaction and the rate of the transformation. By measuring the electric quantities and the rate of reaction, the chemical driving force can be inferred. For example, results for a fuel cell that uses hydrogen and oxygen yield the same value for the chemical driving force as measurements on burning hydrogen. (When hydrogen is burned, we have the same chemical reaction as in a fuel cell operating with hydrogen and oxygen. In contrast to the electrochemical cell where the energy released is used for pumping charge, the only direct result from the burning of hydrogen is the production of entropy.)

Citric acid and baking soda. A small amount of water (about 25 g) with some 7 g of citric acid ($H_3C_6H_5O_7$) dissolved in it is put into a paper cup. The solution is relatively cold (about 16°C, Fig. 6.7). Then, 9 g of baking soda ($NaHCO_3$) are added. There is a strong reaction, gas is produced and escapes (the mass of the solution decreases), and the temperature of the solution decreases quite noticeably. If we wait, the solution gets warmer again.

Interpretation. The reaction of citric acid with baking soda clearly releases energy. This is no different from any other voluntary reaction. Here the energy is used to produce entropy (there are no obvious direct mechanical or electric phenomena resulting from the reaction). Still, the temperature of the solution continues to fall. We conclude that the products of this reaction (sodium citrate, carbon dioxide, and water) take much more entropy than can be produced in the reaction running by itself; in fact, the most important species in this regard is CO_2 which carries away a lot of entropy. Apart from the reaction itself, the solvent (water) is the only other source of entropy. Therefore, its temperature drops. (The environment can provide entropy as well, but it reacts too slowly to compensate for the cooling effect of the escaping CO_2. However, if we wait long enough, we see how the environment heats the solution in the cup: entropy flows in from the surrounding air.)

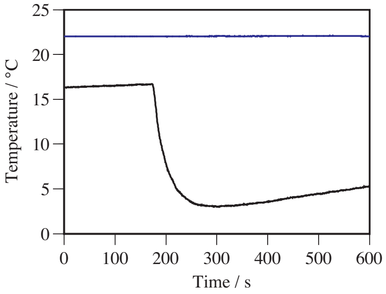

Figure 6.7: Temperature of water with citric acid dissolved in it (first horizontal at 16°C), in a paper cup. At $t = 180$ s, baking soda is added. The upper line at 22°C represents ambient temperature.

When the temperature decreases, the form of the data taken indicates that the reaction proceeds quickly at first and then slows down. This is what has been observed before in reactions (Fig. 6.3) and in many other simple dynamical processes.

The chilling effect of water on your skin. When you step out of the shower you feel colder than if your skin were dry under the same circumstances. Actually, this is true only if the air around you is not too humid. A technical device shows that this phenomenon affects not only living beings. If you place a wet thermometer in air, it shows a lower temperature than if it were dry (the so-called wet-bulb temperature is used to indicate relative humidity of the air). Fig. 6.8 shows data of the temperature of a thermometer that was put in water, removed from it and let dry in the ambient air. The air of the room was rather dry with only 20% of the maximum possible humidity.

Interpretation. What happens first is chemical in nature: If the air surrounding a (wet) body is not totally humid (not fully saturated with water vapor), water will evaporate from the surface of the body. This is explained by saying that the chemical potential of liquid water on the surface of the body is higher than that of the vapor already present in the air. Since there is a chemical driving force between the water and the water vapor, water will evaporate (it goes in the direction of the smaller chemical potential).

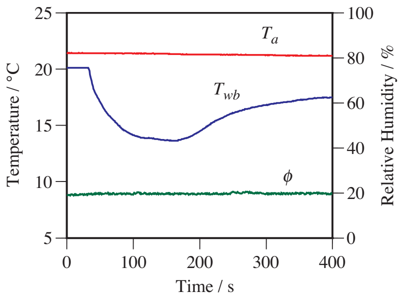

Figure 6.8: Temperature of a wet thermometer (T_{wb}) in air (T_a). The relative humidity (ϕ) of the air is 20%. Initially, the thermometer is in a jar containing water at 20°C. At $t = 20$ s, it is taken out of the water.

Now, evaporation can be considered a chemical transformation. Substance A transforms into substance B. Since energy is released in the process, entropy is produced. So why do we or the thermometer get cold? The case is very similar to that of the fizzing reaction of bicarbonate in citric acid described above (Fig. 6.7). The water vapor that is produced from water contains much more entropy than the stuff it originates from (remember the discussion of phase changes in Chapter 5). The entropy produced simply is not enough; therefore, the water at the surface of the body, and finally the body itself, must provide the entropy of evaporating water. Their temperatures fall.

(The case of the wet bulb thermometer is simpler than that of our bodies. Since the surface temperature of a human body is normally higher than that of the ambient air, we have to take into consideration temperature differences as well as concentration differences.)

Melting ice, freezing water. If an ice cube is placed in a warm environment, it will melt. If water is put in a freezer, it will turn into ice. Actually, the freezing will happen at 0°C, and the melt water will be at that same temperature. When we dissolve salt in water, it will freeze at a temperature lower than 0°C.

Interpretation. When ice has a temperature above 0°C, its chemical potential must be higher than that of water. Conversely, when water is at a temperature below 0°C, its chemical potential must be higher than that of ice at the same temperature. There must be a temperature at which the chemical potentials of liquid and solid H_2O are equal: this is the freezing point. Phase changes take place when the chemical potentials of the phases are equal. The observation tells us that the chemical potential of a substance depends upon its temperature.

At 0°C, ice and water are in chemical equilibrium. If we now dissolve salt in the water, we disturb the balance: the chemical potential of water will be lowered (remember the discussion of osmosis). As a result, ice must melt: H_2O goes from ice into the solution where its potential is now lower. Obviously, the melting point of ice has been lowered by the addition of salt. Salty water on the streets in winter or sea water will melt only at temperatures below 0°C.

QUESTIONS

1. Imagine a certain quantity of hydrogen gas in a container of prescribed volume at a certain temperature. What happens to the pressure if you use the *same mass* of oxygen instead?
2. Why do we have left over substance when we let 1 kg of hydrogen gas react with 1 kg of oxygen gas? Which of the substances will be left over?
3. In what way do chemical reactions suggest a particle image of substances?

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4. Consider the conversion of α-glucose into β-glucose (Fig. 6.3). How can you use the experimental results to motivate the concept of chemical potential.
5. What is the role of energy in a fuel cell or a battery? How does energy get released, what is it used for? How do batteries and fuel cells differ?
6. Explain the basic difference between burning a fuel on the one hand, and letting sodium bicarbonate react with citric acid.
7. Explain the condition of air saturated with humidity (completely humid air) based on the concept of chemical potential.
8. What happens to the temperature of the boiling point of water if salt is added? (Hint: Consider water and water vapor in equilibrium at the normal boiling point. Now add salt to the liquid phase. What happens?)

6.2 TWO DYNAMICAL MODELS

Let me introduce two simple dynamical models that transform the ideas behind our word models of chemical processes into quantitative relations. The models will have structures similar to the ones we have expressed before.

Toluene in water and air. Consider an example similar to the one discussed in Fig. 6.2, the diffusion of toluene in the environment. Let there be only water and air in contact, with some toluene in the water initially. Our model should start with an expression of the balance of amount of substance of toluene in water and air (Fig. 6.9). The important job is now to find expressions for the driving force of the transport and the flow of toluene.

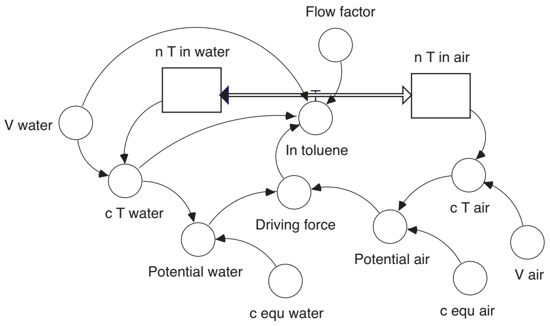

Figure 6.9: Diagram of a system dynamics model of the transport of toluene from water to air or vice-versa.

The flow should be made dependent upon the chemical driving force. Let us imagine this force to be an intrinsic tension. This means that the flow should also be proportional to the amount of toluene (which is in the water); if there is more stuff, more will be flowing per unit tension. The simplest expression that corresponds to these ideas is

$$I_{n,Toluene} = -k_n V_w c_{Tw} \mathcal{A} \tag{6.1}$$

I_n is a current of amount of substance, k_n is a chemical flow factor, and $\mathcal{A}$ symbolizes the chemical driving force (the symbol $\mathcal{A}$ is inspired by the old term *affinity*). V and c are volume and concentration, respectively. The driving force is equal to the chemical potential difference of toluene in the two environments. The potentials will obviously depend upon the concentrations of the dissolved substance, but how? In the case of diffusion in a uniform environment, we could simply use the concentration and thus make the driving force depend upon the concentration difference. This does not work here—toluene prefers to be in water by a factor of four (Fig. 6.2). Here is an idea we can try: Make the potential proportional to the relative concentration, relative to the equilibrium concentration in the particular environment. So we can say that

$$\mathcal{A} = \frac{c_{Tw}}{c_{Tw}^{eq}} - \frac{c_{Ta}}{c_{Ta}^{eq}} \tag{6.2}$$

$\mathcal{A}$ is the chemical driving force. Here, I simply set the constant of proportionality equal to one. T stands for toluene, w and a for water and air respectively, and eq denotes equilibrium.

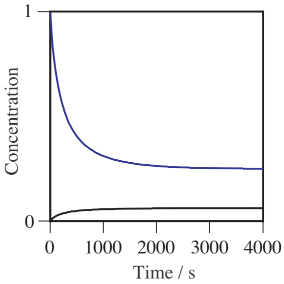

Figure 6.10: Simulation results for the model in Fig. 6.9. Concentration is arbitrary.

The rest of the model is standard. With numbers for initial concentrations and equilibrium values taken from Fig. 6.2, we obtain results like the one in Fig. 6.10. I had to adjust the volume of air to about twelve times the volume of water, and find a flow factor that gives us a behavior over time similar to the one observed. Note that we should not directly compare with data in Fig. 6.2 since that case involved toluene in soil as well. All I want to point out is the similarity and the fact that, as observed, we do get different concentrations at equilibrium.

Radioactive decay of silver. Many isotopes of elements are unstable, they decay radioactively. This is a well known phenomenon, it has almost archetypal dynamics—the number of radioactive nuclei decays exponentially. Since the decay rate is assumed to be proportional to the amount of substance, the number of decays per unit time (which can be measured with counters) also decreases exponentially. Fig. 6.11 shows data of the decay of radioactive silver and simulation results of the model I am going to create here.

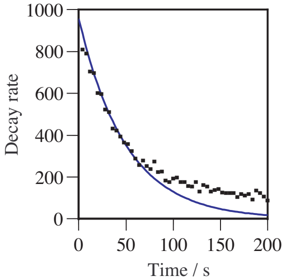

Figure 6.11: Simulation results for the model in Fig. 6.12, and data of decay rate of two silver isotopes, ^{110}Ag and ^{108}Ag (L. Wickham). The difference between model and data (starting around 100 s) results from a second radioactive isotope of silver that is present in the sample; the model takes into account only ^{110}Ag. If the second were included as well, agreement would be nearly perfect.(^{108}Ag decays much more slowly, and there is less of it present originally.)

Let us see if ideas similar to the ones just used can lead to a useful model of radioactive decay. We start again with an expression of the law of balance of amount of silver isotopes (see Fig. 6.12):

$$\frac{dn_{Ag}}{dt} = \Pi_{n,Ag} \tag{6.3}$$

The reaction rate Π_n is the rate of production of silver (here, the quantity must be negative, it is a rate of destruction). It is assumed that the species decays as the result of a single process, is not produced by some other process and does not flow. The important task is to model the decay rate (reaction rate). If we use reasoning similar to the one applied to the flow of a substance, we should argue that the decay rate must be proportional to the amount of substance and the chemical driving force (Fig. 6.12):

$$\Pi_{n,Ag} = -kVc_{Ag}\mathcal{A} \tag{6.4}$$

As in the previous case, we might want to make the chemical potentials of the substances involved dependent on the (relative) concentration. Here, however, the similarity with ordinary chemical processes ends. The chemical potentials of nuclear materials is virtually unaffected by density and temperature—unless these take extreme values such as ones found in some stellar interiors. In other words, the potentials, and the chemical driving force with them, are basically constant. If we accept this idea, we get good agreement between models and reality (Fig. 6.11).

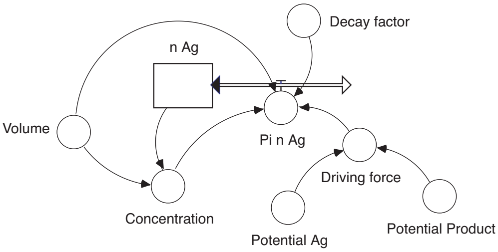

Figure 6.12: Diagram of a system dynamics model of the radioactive decay of a silver isotope. Note that the chemical potentials are independent of concentration.

6.3 THE CONCEPT OF AMOUNT OF SUBSTANCE

Physical systems "possess" certain fundamental properties: a body has mass, entropy, momentum (if it moves), and electric charge (if it is not electrically neutral), to name some of the most important. This section will describe another basic property, namely amount of substance. Amount of substance is by no means a replacement for mass, or just a convenient means of bookkeeping for chemists. Every physical system, be it matter or light, has this property, and there are physical phenomena associated with its existence.

First, we introduce the relation of amount of substance to mass (and by implication, to volume) and measures derived from amount of substance. The latter quantities (molar quantities, densities, concentrations) are of practical importance for using amount of substance in chemical relations. The law of balance of amount of substance is then formulated for processes of flow and reaction in homogenous systems.

6.3.1 Substances, Chemical Reactions, and Electrolysis

The numerous substances undergoing a myriad of processes of material transformation furnish the first indication of the existence of the quantity called amount of substance. Chemical reactions and electrolysis will be described briefly after we look at what constitutes a basic or an elemental substance.

Basic substances. The many material objects known to us usually are composed of different substances which we call *basic* in the sense that we can explain the material make-up of objects in terms of a mixture of these constituents. Now, there are several levels of *fundamental building blocks*, where the levels are defined by those investigating the objects. For a particular cook, it might suffice to know that a Thai green curry consists of green curry paste, chicken, coconut milk, and some vegetables; while another cook will only be satisfied by knowing how the green curry paste is composed of "basic" foods. A biologist will want to know how the Thai eggplant in the curry is made up of cells; a biochemist might stop only at the level of the pure chemical substances constituting a part of a cell or might even want to know which chemical elements these substances are made up of. If these various levels of what different people call *fundamental* are not enough, consider the viewpoint of physicists, who are concerned with the structure of atoms in terms of electrons, protons, and neutrons.

To describe the composition of an object from more fundamental constituents, different forms might be used. Common to all these is some way of telling "how much" of each of the building blocks occurs in the system under investigation. The composition of dough for bread might be described as

$$\mathit{flour}_3\mathit{water}_2\mathit{yeast}_{0.1}\mathit{salt}_{0.05}$$

where the subscripted numbers denote amounts of each substance measured in cups. Granite could be described by

$$A_{v1}B_{v2}C_{v3}\ldots$$

where A, B, and C denote the various minerals making up the rock, and the numbers $v1$, $v2$, and $v3$ measure the relative volume of each of the constituents. Chemists use the elements as their basic building blocks, which means that chemical substances are understood in terms of their composition written in the form

$$\mathrm{C_2H_5OH}$$

(for ethyl alcohol) where the letters stand for the chemical elements, and the numbers give the amount of substance of each of the elemental substances. The rest of this section is devoted to clarifying the latter concept. For physicists, finally, one unit of amount of substance of pure helium-4 could be written as

$$p_2n_2e_2$$

In this expression, p, n, and e stand for the substances called protons, neutrons, and electrons, respectively,[2] and the formula tells us that two units of amount of substance of each of the three building blocks make one unit of helium-4.

Chemical reactions and the amount of substance. We can approach the concept of amount of substance by studying chemical reactions. By going through a multitude of different reactions, we find that pure chemical substances in mixtures undergo complete reactions only if their amounts occur in special proportions (Section 6.1). *Complete* means that the species are used up completely. Lacking the concept of amount of substance, we have to start with some other measure of the amount of a species, for which we take its mass.

If we count 2 g of hydrogen gas as *one unit of amount of substance*, called 1 mole, the reactions in Fig. 6.1 tell us that 1 mole of hydrogen gas (H_2) has a mass of 2 g, 1 mole of oxygen gas (O_2) has a mass of 32 g, while the mass of 1 mole of chlorine (Cl_2) is 71 g. The mass of one mole of amount of substance is called the *molar mass* M_0 of the substance, and is defined by

$$m = M_0 n \tag{6.5}$$

These observations carry over to all elemental substances and pure chemical substances. There are always constant and multiple proportions of the amounts of the constit-

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[2] We do not have names for the substances whose "atoms" are the proton, neutron, and electron, respectively. The names are used for the particles rather than for the substances. Neutron stars, for example, are made up of the n-substance.

uents involved in complete reactions. A complete reaction is our way of defining what we mean by equivalent amounts of substances in a chemical sense. Equivalent amounts are determined by the phenomena involving chemical transformation, and not, as we might believe from our everyday usage of the term, by the phenomena of gravity quantified in terms of (gravitational) mass.

Naturally, much more experience is required with chemical reactions than the three examples provided above in Fig. 6.1, if we want to figure out how much of a substance is equal to one unit of amount of substance. The examples used display some complexity in that we would have to answer the question of why hydrogen gas is H_2 and not H, and why 1/2 mole of oxygen gas (and not 1/3, or 2, or 3 mole) reacts completely with one mole of hydrogen gas to form one mole (and not 1/2, or 2 mole) of water. Part of the experience which tells us more about equivalent amounts of substance actually comes from physical phenomena involving gases.

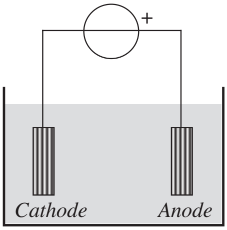

Figure 6.13: In electrolysis, chemical substances may be transformed when electric charge is passed through them. In a melt of potassium chloride, for example, potassium is deposited at the cathode as long as the current is flowing.

Electrolysis. The combination of chemical reactions with electricity provides another strong indication of the special property measured in terms of amount of substance. In electrolytic reactions, electrical currents passing through conducting fluids are responsible for chemical transformations. Multiple proportions of electric charge are needed for multiple units of amount of substance to appear at the electrodes. Take the examples of the electrolysis of potassium chloride (KCl) and of copper chloride ($CuCl_2$). It is found that a certain amount of charge has to be passed through the molten salt of KCl to deposit 1 mole of potassium at the cathode, while it takes exactly twice this charge to deposit 1 mole of copper. The reactions involved are

$$\begin{aligned} K^+ + e &\rightarrow K \\ Cl^- &\rightarrow 0.5Cl_2 + e \end{aligned}$$

for potassium chloride, and

$$\begin{aligned} Cu^{2+} + 2e &\rightarrow Cu \\ 2Cl^- &\rightarrow Cl_2 + 2e \end{aligned}$$

for the electrolysis of copper chloride. Here, e again stands for the substance called electrons. These phenomena can be summarized in the relation

$$Q = z \mathcal{F} n \qquad \textbf{(6.6)}$$

An amount of substance n requires an amount of charge Q for electrolysis which is determined by Faraday's constant $\mathcal{F}$ = 96487 C/mole, and a (small) positive or negative integer number z (the charge number).

What we should learn from this is what we have seen before: it is not the mass of a substance which scales simply with fixed amounts of electric charge involved; rather, it is the same quantity introduced above as a measure of equivalent amounts of a substance, namely the fundamental property called amount of substance.

EXAMPLE 6.1. Electrolysis of copper chloride.

A current of electric charge of 10 A is passed through melted copper chloride for one hour. How much copper will be deposited at the cathode?

SOLUTION: The amount of charge passed through the melted substance is calculated from the current:

$$Q = I_Q \Delta t = 10\,\text{A} \cdot 3600\,\text{s} = 3.6 \cdot 10^4\,\text{C}$$

With $z = 2$ for copper ions, Equ.(6.6) yields

$$n = \frac{Q}{z\mathcal{F}} = \frac{3.6 \cdot 10^4\,\text{C}}{2 \cdot 96487\,\text{C/mole}} = 0.187\,\text{mole}$$

which, with a molar mass of 0.0636 kg/mole for copper, is equivalent to $1.19 \cdot 10^{-2}$ kg of copper.

6.3.2 Amount of Substance and Particles

The foregoing discussion is often cast in the form of a microscopic model of matter. Matter is said to be composed of particles (which, for the chemist, might be atoms or molecules), and the amount of substance is interpreted as the number of particles of the substance in question. The number of particles appearing in 1 mole of a substance is called Avogadro's number, and it can be calculated from different types of measurement. Let me mention only one measurement, which takes electrolysis as the starting point. Since we also have a microscopic model of charge, the "atom" of charge being the elementary charge ($e = 1.6022 \cdot 10^{-19}$ C), we may say that we need an integer number of elementary charges for each particle of the substance being electrolyzed and deposited at one of the electrodes. If we call τ the *atom of amount of substance*, i.e., the *elementary amount of substance*, and N is used for the number of particles as well as for the number of elementary charges, then Equ.(6.6) can be transformed into

$$Ne = z\mathcal{F}N\tau \tag{6.7}$$

With $z = 1$ we obtain a value of

$$\tau = \frac{e}{\mathcal{F}} = \frac{1.6022 \cdot 10^{-19}\,\text{C}}{96485\,\text{C/mole}} = 1.661 \cdot 10^{-24}\,\text{mole} \tag{6.8}$$

for the smallest amount of substance possible. This translates into $N_0 = 6.022 \cdot 10^{23}$ particles per mole of a substance (Avogadro's constant).[3]

6.3.3 Molar Quantities and Measures of Concentration

Substances are spread out through space and other substances, they appear alone or with one or several other species. In order to get a handle on amounts of the various

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[3] In general, we should be careful with the "particulate" interpretation of the structure of matter. The values of e and τ are understood in terms of quantum theory as the quanta of electric charge and amount of substance, respectively. Thinking of little particles roaming around in empty space might be handy but can be misleading at times. Especially the microscopic picture of the ideal gas as a swarm of free particles does not help much in understanding the behavior of dilute solutions where the particles certainly are not free. And in the case of light it turns out that the quanta of amount of substance of light are not photons but rather combinations of photons.

substances, we use densities, molar quantities and different measures of concentration, especially in the case of solutions (solutes dissolved in a solvent). Here, some of the measures useful for our purpose will be defined.

Molar quantities. Quantities that are stored in materials or that are otherwise fluidlike—such as entropy, mass, charge, volume—can be related to the amount of substance of the body. We use small letters with an overstrike to denote the molar quantities. Here are *molar entropy* and *molar volume*:

$$\bar{s} = S/n \quad , \quad \bar{v} = V/n \tag{6.9}$$

The well known *molar mass* is defined analogously:

$$M_0 = m/n \tag{6.10}$$

Concentration measures are used to indirectly express the amounts of substance of a particular species—the solute—dissolved in a solvent. There are many different measures called *concentration*.

Mass fraction and molar (or mole) fraction. The *mass fraction* of a solute in a solution is defined as the mass of the solute (s) of a species divided by the total mass of the solution (solvent f and solute s):

$$x_s = \frac{m_s}{m_f + m_s} \tag{6.11}$$

The definition also applies to the solute so that the sum of the mass fractions of solvent and solute(s) always equals 1. The ratio of the amount of substance of a dissolved species (the solute) and the total amount of substance of the solution is called the *molar fraction*:

$$\bar{x}_s = \frac{n_s}{n_f + n_s} \tag{6.12}$$

The definitions show that mass and molar fractions are dimensionless. Again, we can apply the definition to the solvent as well.

Mass-volume fraction. This is the ratio of the mass of the solute and the volume of the total solution (even though it looks suspiciously like the standard density, it should not be confused with this concept):

$$z = m_s/V_{solution} \tag{6.13}$$

Molar concentration (molarity), molality and molinity. This is the standard measure of concentration used in much of the following. It is defined as the amount of substance (dissolved) divided by the total volume of the solution:

$$\bar{c}_s = n_s/V_{solution} \tag{6.14}$$

The unit of the molar concentration (molarity) is mole/m^3. Note that the value commonly used for the standard state is mole/L (L: liter); this unit has its own abbreviation: mole/L = M.[4] Finally, the terms *molality* and *molinity* denote the ratio of amount of substance to the mass of the solvent (molality, symbol m_B) or the total mass of the solution (molinity; no symbol). Both have the unit mole/kg.

EXAMPLE 6.2. Table salt (NaCl) in water.

100 g of table salt (NaCl) are dissolved in 1.0 L of water. (a) Determine the molality and molinity of the solution. (b) What is the (molar) concentration? (c) What are the mass and molar fractions?

SOLUTION: Table salt has a molar mass of 0.0585 kg/mole. So there is n_s = 0.100 kg / 0.0585 kg/mole = 1.71 mole of salt. For water we get n_w = 1.0 kg / 0.018 kg/mole = 55.5 mole.

(a) The molality is m_B = 1.71 mole / 1.0 kg = 1.71 mole/kg. The molinity turns out to be equal to 1.71 mole / 1.100 kg = 1.56 mole/kg.

(b) On the basis of what we have discussed so far, we cannot determine the molar concentration accurately since we do not know what happens to the volume of the solution when 100 g of salt are dissolved in 1.0 L of pure water. Assuming that the volume does not change much, we can get an estimate: $c \approx$ 1.71 mole / 1 L = 1.71 mole/L.

(c) x = 0.100 kg / (1.000 kg + 0.100 kg) = 0.0909. $\bar{x}$ = 1.71 mole / (55.5 mole + 1.71 mole) = 0.0299.

6.3.4 Balance of Amount of Substance

Amount of substance—the formal measure of amounts of "stuff"—is visualized rather easily, certainly more easily than say, momentum, entropy, or charge. It is almost as intuitive as amounts of water or money. So it should be relatively simple to formulate the law of balance of amount of substance.

Law of balance for systems with transports. If only transports are allowed, the amount of substance (symbol n; unit: mole) stored in a system changes only because of flow of amount of substance I_n. Basically, there are two types of transport of a species. A substance may flow in by diffusion, or it may be transported by a fluid it is dissolved in (in this case, the fluid enters or leaves the system as well). The former is a *conductive transport*, whereas the latter may be termed *convection*. If we are interested in a pure fluid entering a system, we may speak of bulk transport which can be included with convection.

The sum of all flows determines the rate of change of n:

$$\dot{n} = I_{n,cond} + I_{n,conv} \tag{6.15}$$

The units of currents of amount of substance are mole/s. There are many different chemical species in nature. This means that we have to write a law of balance independently for each substance that is relevant in a particular application.

Law of balance for reactions. Reactions lead to the destruction or production of chemical species. When hydrogen reacts with oxygen to form water, hydrogen and ox-

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4. One may speak of a "2 M solution," meaning that two moles of a substance have been dissolved in 1 L of the solution (not 1 L of solvent!). This can be confusing because M is officially supposed to be used as the *symbol* of molarity. So we should rather say M = 2.0 mole/L.

ygen disappear and water appears. A process of production (or destruction) is described in terms of a *production rate* Π_n (analogous to the production rate of entropy in thermal processes). A substance may be produced (or destroyed) simultaneously by different reactions. The rate at which the amount of a certain substance changes is determined by the sum of all production rates:

$$\dot{n} = \Pi_{n,net} \tag{6.16}$$

Again we have to write such an equation for every species of interest. The unit of a production rate of amount of substance is mole/s.

General law of balance. If transports and reactions are both allowed, the rate of change of the amount of substance of a particular species is determined by the sum of all flows and all production rates (Fig. 6.14). Therefore we have

$$\dot{n} = I_{n,cond} + I_{n,conv} + \Pi_{n,net} \tag{6.17}$$

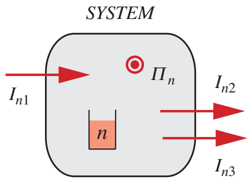

Figure 6.14: Graphical representation of the general law of balance of amount of substance. Substances can be transported, and they can be produced or destroyed.

Relationship between production rates in a reaction. A reaction that uses up all its reactants can be described in terms of a reaction equation containing stoichiometric coefficients. These coefficients are an expression of the "conservation of elements" in a reaction which places a restriction upon the production and destruction rates pertaining to the different species undergoing the transformation. If we write the reaction as

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \quad \rightarrow \quad \upsilon_1 B_1 + \upsilon_2 B_2 + \ldots \tag{6.18}$$

we can say that during the time span the reaction is allowed to run, ν_1 units of A_1, ν_2 units of A_2, etc., are consumed, whereas υ_1 units of B_1, υ_2 units of B_2, etc., are produced.[5] So the relation between the destruction rates of the A's and the production rates of the B's must be

$$\frac{1}{\nu_1}\Pi_{A1} = \frac{1}{\nu_2}\Pi_{A2} = \ldots = -\frac{1}{\upsilon_1}\Pi_{B1} = -\frac{1}{\upsilon_2}\Pi_{B2} = \ldots \tag{6.19}$$

QUESTIONS

9. If one mole of H_2 gas and one mole of O_2 gas have a mass of 2.0 g and 32 g, respectively, what is the molar mass of water?
10. If 100 g of sugar are dissolved in 1.0 L of water, what is the mass fraction of sugar?
11. If 1.0 kg of H_2 gas and 10.0 kg of O_2 gas are brought into a reactor, how much of either substance will be used up in the reaction that produces water? How much water will be produced assuming a complete reaction?
12. Alcohol is transferred into the liver. The current of amount of substance is 0.010 mole /

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[5] A chemical reaction can run both ways. This is sometimes expressed by using a double arrow in the reaction equation Equ.(6.18). Conditions such as temperature and pressure and the presence of other substances can greatly influence the chemical potentials of the species involved in a reaction. As a result, the chemical driving force of a reaction can change its sign (Section 6.4). Here, I simply wanted to be able to speak of reactants and products of a reaction without having to worry about which is which.

min. If the liver makes alcohol decompose at a rate of – 0.0040 mole/min, what is the rate of accumulation of alcohol in the liver? What are these quantities on mass basis?

13. The substance α-glucose transforms into β-glucose (Fig. 6.3). If the production rate of α-glucose is $-\,1.0 \cdot 10^{-6}$ mole/s, what is the production rate of β-glucose?

EXAMPLE 6.3. Sodium bicarbonate reacting with citric acid.

When sodium bicarbonate ($NaHCO_3$) reacts with citric acid ($H_3C_6H_5O_7$) in an aqueous solution, carbon dioxide, water, and sodium citrate ($Na_3C_6H_5O_7$) are formed. (a) Write the reaction equation in a form where the stoichiometric coefficient of citric acid is equal to 1. (b) When one mole of sodium bicarbonate is used up, how much citric acid must have been destroyed? How much carbon dioxide has been formed? (c) Sketch a diagram of a system dynamics model just for the laws of balance of amount of substance. (Assume the destruction rate of citric acid to be determined separately by a constitutive law.) (d) At a moment when the rate of destruction of citric acid is – 0.050 mole/s, what are the other production and destruction rates? (e) For the values in (d), what is the rate of destruction of mass for citric acid and sodium bicarbonate?

SOLUTION: (a) By counting the number of atoms for each element appearing on either side of the reaction equation, we can determine the missing stoichiometric coefficients:

$$H_3C_6H_5O_7 + 3NaHCO_3 \rightarrow Na_3C_6H_5O_7 + 3CO_2 + 3H_2O$$

(b) For one mole of citric acid, three moles of bicarbonate are used. Therefore, for one mole of bicarbonate, 1/3 mole of citric acid will be use up. Since the stoichiometric coefficients for bicarbonate and CO_2 are equal, one mole of carbon dioxide is produced for every mole of bicarbonate consumed.

(c) Rectangles and thick arrows represent stored quantities and flows and reaction rates, respectively. If one reaction rate in a balanced reaction is known, all other reactions rates are determined as well by the stoichiometric coefficients; this is demonstrated by Equ.(6.19). It is assumed that the initial amount of substance for citric acid (CA) is given. Those for CO_2, H_2O and sodium citrate (SC) are equal to zero. Sodium bicarbonate is added at the beginning of the experiment (In_BC).

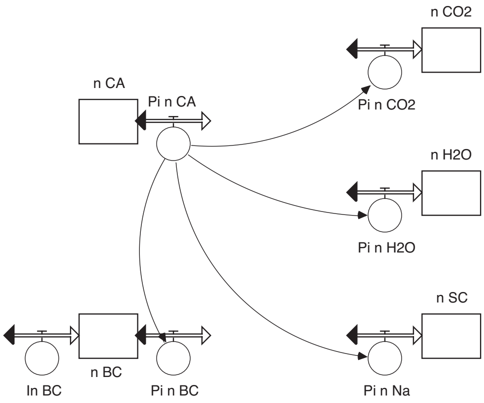

Figure Ex.3

(d) The production and destruction rates are determined relative to that of citric acid (CA) by the stoichiometric coefficients:

Pi_n_BC = 3·Pi_n_CA = – 0.15 mole/s
Pi_n_CO2 = –3·Pi_n_CA = 0.15 mole/s
Pi_n_H2O = –3·Pi_n_CA = 0.15 mole/s
Pi_n_SC = –1·Pi_n_CA. = 0.05 mole/s

(e) The production rate of amount of substance and mass are related as amount of substance and mass, i.e., by Equ.(6.10):

$$\Pi_m = M_0 \Pi_n$$

So we have $\Pi_{m,\mathrm{CA}} = 0.192 \cdot (-0.050)$ kg/s = – 0.0096 kg/s; the second value turns out to be $\Pi_{m,\mathrm{BC}} = 0.084 \cdot (-0.15)$ kg/s = – 0.0126 kg/s.

6.4 CHEMICAL POTENTIAL AND CHEMICAL DRIVING FORCE

Chemical change is ubiquitous. Active ingredients of medication decay with time as do the radioactive elements in the Earth's crust. Hydrogen inside the Sun changes into helium, vapor in the air condenses to form fog, and the chemicals inside a battery change when they drive a current of charge through wires. We would like to cast this tendency of substances to change in the form of a physical principle. You certainly remember the questions of why water flows or what makes heat flow. In the same manner, we will ask what makes chemical species change. Why do some chemical reactions take place while others do not? Why does a particular substance flow from place A to place B while another does not? Why does a substance change its phase, go from liquid to solid or from liquid to gaseous, rather than from solid to liquid, etc.?

6.4.1 From Experience to Concept

One element of the description of physical processes are intensive quantities that are used to quantify driving forces. Temperature and pressure are the potentials of thermal and fluid processes, respectively, and we view temperature and pressure differences as driving forces. Chemical transformations are no different; the phenomena discussed in Section 6.1 testify to the success of this conceptualization. A summary of those examples will prepare the ground for a more formal introduction to chemical potentials and chemical driving forces.

Section 6.1 demonstrates that the idea of a chemical driving force applies to an extremely rich field of phenomena ranging from transport to change of substances where change includes phenomena not commonly listed as such. These include solutions and phase change. Simply said, whenever there is a process involving substances rather than charge, entropy, momentum or volume, we should be looking for a chemical driving force.

Remember how transport processes were described. A dye diffuses through gel from places where its concentration is high to where it is low; we say that the chemical potential of the dye is higher where it is more concentrated and, in different words, that there is a chemical driving force because of the difference of chemical potentials at two points. When a substance that could diffuse does not, there is either such a high barrier that it prevents what would normally happen or the chemical driving force is simply equal to zero. The latter condition is called equilibrium. The diffusing substance is in equilibrium at different locations. Remember that this condition need not mean that the concentration of the substance is the same everywhere. It may well be, as in the case of toluene in water and air (Fig. 6.2), that equilibrium is attained when concentrations in the two media have attained a particular ratio. We say that in this case the chemical potentials have become equal and toluene no longer migrates from one environment into the other.

An important transport process is osmosis, particularly in biological environments. When red blood cells, dried lentils, or potato cores are placed in pure water, they swell (Fig. 6.4). Water flows into the cells since there are substances dissolved in the intracellular fluid. This is explained by saying that the chemical potential of water inside the cells is lower than outside. The potential of water (as a solvent) is lowered by dissolving substances in it which can also be interpreted as lowering the concentration of water. If we salt the water heavily and thereby lower its chemical potential before placing potatoes in it they may shrink instead of grow (Fig. 6.4).

Explanations for chemical reactions are analogous. In a spontaneous reaction, we say that the chemical potentials of the participating substances are such that the reaction "runs downhill" as does entropy as it flows conductively through a temperature gradient. We might say that substances "prefer" to be in the form of products, or that there is a chemical driving force from reactants to products. When pure α-glucose is dissolved in water, some of it converts spontaneously into β-glucose (Fig. 6.3). There must be a chemical potential difference driving the reaction. As the reaction progresses, the chemical potential of α-glucose decreases—since its concentration decreases—while that of β-glucose increases. When a particular ratio of concentrations has been attained, the chemical reaction stops. We say that the chemical potentials of the two substances have become equal, the driving force is zero and equilibrium has been established.

Dissolving substances in solvents—CO_2 in water, O_2 in blood, salt in water—and phase changes present us with more examples of chemical transformations that can be explained in analogy to how I just described transports and reactions. To give just one example, as we increase the concentration of CO_2 in the atmosphere by burning fossil fuels, the chemical potential of this component is increased. We should therefore expect that at least some of it dissolves in the oceans where the CO_2 concentration is initially unchanged: there is a chemical driving force for CO_2 to go into solution until a new equilibrium has been established (there are many possibilities for changing the chemical potential of dissolved carbon dioxide in sea water, not just a change of its concentration; an important factor is the temperature of the water taking up CO_2, another is pressure which changes greatly with depth in the oceans).

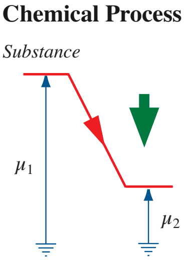

Figure 6.15: Waterfall image of a spontaneous chemical process: A substance falls from a point of high chemical potential μ_1 to a point of lower chemical potential μ_2, thereby releasing energy at a well defined rate.

Spontaneous and driven chemical change. There is an important aspect of chemical change as indeed there is of any kind of physical process. Sometimes a process runs spontaneously, sometimes it does not. The notion of a chemical driving force most aptly expresses this distinction in a different way. A spontaneous chemical transformation—transport, solution, phase change, reaction—goes in the direction of decreasing chemical potential (Fig. 6.15). A non-spontaneous change simply goes the other way, meaning that the driving force has changed its sign.

As we know from our discussions of physical phenomena, the concept of spontaneous or driven process is related to energy. Energy is released if a process "runs downhill." So a (chemical) process is spontaneous going from high to low potential because energy can be released. Energy made available in a process can in turn drive chemical substances "uphill" through a chemical potential difference (see Section 6.5).

6.4.2 The Driving Force of Simple Chemical Conversions

The foregoing discussions should have made the idea of chemical potential and chemical driving force clear. What remains to be done is formalizing the concept, using it and the determining actual values of potentials and driving forces. This will be done in much of the rest of this chapter. Here is a first step in this direction.

In summary, the *chemical potential* measures the *tendency of substances to transform, i.e., to change or to migrate*. It is analogous to pressure, electrical potential, gravitational potential, or temperature (Fig. 6.16). Differences of the chemical potential act as *driving forces* of chemical processes. Each substance has a chemical potential that may depend upon a number of factors such as temperature, pressure, concentration, environment etc. The process of migration of a species is depicted as its flow from points of high to points of low potential (Fig. 6.16, left), whereas the conversion of a substance A into a substance B is visualized as the disappearance of the former at a high level and the appearance of the latter at a lower level (Fig. 6.16, right).

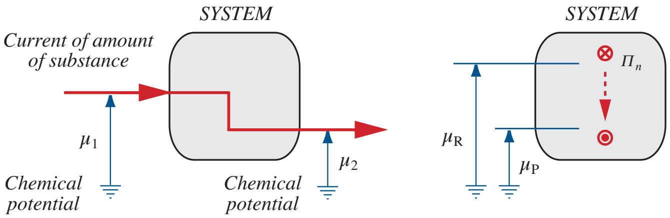

Figure 6.16: Process diagram for flows of amount of substance. (left) or destruction and production of species (right). The chemical potential (μ) is like the level of a substance. Differences of chemical potentials denote driving forces of the transport of a species. μ_R and μ_P represent potentials of reactants and products, respectively.

Simple transformations. To introduce a more formal description of chemical driving force let us consider only the simple transformation of a single substance into another single species. This can be written as a reaction equation:

$$A \rightarrow B \tag{6.20}$$

Examples of such conversions are the melting of ice, mutarotation of glucose, diffusion of a dye from one point to another, sugar dissolving in water, evaporation of mercury in air, the decay of an atom or a nucleus from an excited state (if we do not include photons emitted as another substance), etc. We call μ_A and μ_B the chemical potentials of substances A and B or of a substances in state or location A and B. Then the *chemical potential difference* for the transformation is

$$[\Delta\mu]_{A\rightarrow B} = \mu_B - \mu_A \tag{6.21}$$

Chemical driving force. Basically, the chemical driving force of a transformation is its chemical potential difference. However, as in electricity where negative electric potential differences denote voltages (Chapter 1), we introduce the negative of the chemical potential difference and call it the *chemical driving force* $\mathcal{A}$:

$$\mathcal{A}_{A\rightarrow B} = -[\Delta\mu]_{A\rightarrow B} \tag{6.22}$$

According to our convention, a positive driving force (negative potential difference) is associated with a spontaneous chemical conversion, whereas a non-spontaneous transformation is associated with a negative driving force (Fig. 6.17).

Spontaneous
transformation $\mathcal{A} > 0$

Non - spontaneous
transformation $\mathcal{A} < 0$

Figure 6.17: Chemical driving force of spontaneous or non-spontaneous conversions.

Equilibrium. Typical transformations—reactions and transports—run and then stop. When they are finished, equilibrium has been established (analogous to equilibrium in communicating containers, or to thermal equilibrium for bodies in thermal contact). For chemical reactions, the *condition of equilibrium* is

$$\mathcal{A}_{A \to B} = 0 \tag{6.23}$$

Processes can be started on either side of equilibrium, meaning that a reaction can run in both directions of a reaction equation. Reactions can be driven away from equilibrium by “intervention” (a battery can be recharged by applying an external electric voltage).

6.4.3 Some Examples and Applications

We will study simple examples to familiarize ourselves with some values of chemical potentials and their use. For now, we will accept values of potentials without worrying where they come from. The source of actual numbers will become clearer as we move deeper into the theory of chemical processes.

Nuclear decay. Let me begin with the example of the spontaneous transformation of one species into another, such as the decay of a molecule or the radioactive decay of an isotope (if we neglect “small” by-products). Here we most clearly see the innate tendency, or drive, to change. Change takes place until a form of matter is found which is stable. It is like water flowing downhill, over steps, until it reaches a place from which there is no possibility of falling further.

Take the example of strontium-90 decaying into yttrium-90, which decays further into zirconium-90. The answer to the question of why, for example, yttrium does not change into strontium would be simple: of the two possible reactions

$$^{90}\mathrm{Sr} \rightarrow {}^{90}\mathrm{Y} \quad , \quad {}^{90}\mathrm{Y} \rightarrow {}^{90}\mathrm{Sr}$$

only the former would take place spontaneously. This means we imagine each isotope to be at a certain chemical level, i.e., as having a certain chemical potential (Fig. 6.18). Now, Sr-90 must be at a higher level than Y-90, and this isotope is at a higher level than Zr-90.

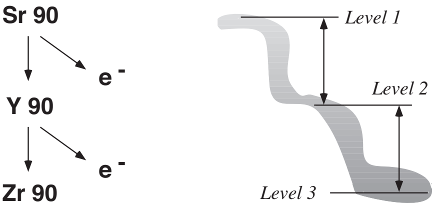

Figure 6.18: Decay of one substance into another is like a ball rolling down a hill or water falling over rocks. In each case, we explain why the processes are taking place by calling upon the concept of a driving force.

Approximate values of the chemical potentials of the isotopes discussed here are given in Table 6.1. They are $8.080505 \cdot 10^{15}$ G for Sr-90, $8.080453 \cdot 10^{15}$ G for Y-90, and $8.080231 \cdot 10^{15}$ G for Zr-90. G (Gibbs = Joule/mole) is the unit of the chemical potential. The chemical potential differences are $-52 \cdot 10^9$ G and $-222 \cdot 10^9$ G, respectively. The drop from strontium to yttrium is about four times smaller than the drop from yttrium to zirconium. If all else were equal, we might expect the second transformation to be more intensive or run more quickly which indeed it does. However, the half-lives are 28.9 years and 2.67 days, respectively, so their ratios indicate that other factors must play an important role in the speed of reactions as well.

Table 6.1: Absolute chemical potentials of some isotopes

Isotope	M_0 / kg/mole	μ_0 / kG
^{1}H	0.001007825	$0.0905788 \cdot 10^{12}$
^{4}He	0.004002603	$0.359736 \cdot 10^{12}$
^{90}Sr	0.08990774	$8.080505 \cdot 10^{12}$
^{90}Y	0.08990716	$8.080453 \cdot 10^{12}$
^{90}Zr	0.08990470	$8.080231 \cdot 10^{12}$

The values in Table 6.1 show two things. Chemical potentials are absolute (Section 6.5.4), and their basic values are determined from the (molar) mass of a substance which is equal to the molar energy. This is another indication of the role of energy in chemical processes which will be studied in Section 6.5.

Chemical reactions. Since each substance has its drive, i.e., its chemical potential, the question of whether a particular reaction takes place is answered by whether the potential of the product is lower than that of the original substance. For example, hydrogen (H_2) and oxygen (O_2) are both given a chemical potential of 0 kG. Water, on the other hand, is found to have a chemical potential of – 237 kG (see Table 6.2). Therefore, the spontaneous reaction (first reaction in Fig. 6.19) would have to be the one where water forms out of the substances that contain only the elements; this is indeed what we observe. The (necessary) condition for a reaction to occur therefore is that the change of the chemical potential has the proper sign: it must be negative; a spontaneous reaction goes “downhill.” Note that in contrast to the values for isotopes, the chemical potentials given here are relative. How zero points of chemical potentials are defined, will be discussed in more detail in Section 6.5.

$$\underbrace{H_2 + 0.5O_2}_{0\,\mathrm{kG}} \rightarrow \underbrace{H_2O}_{-237\,\mathrm{kG}}$$

$$\underbrace{HgJ_{2,\mathrm{yellow}}}_{-100.1\,\mathrm{kG}} \rightarrow \underbrace{HgJ_{2,\mathrm{red}}}_{-100.8\,\mathrm{kG}}$$

Figure 6.19: The reaction which forms water out of the elemental substances is spontaneous: it corresponds to a decrease (negative change) of the chemical potential. The reverse reaction does not occur spontaneously. Freshly prepared (yellow) mercuric iodide spontaneously changes from its yellow to its red modification.

Table 6.2: Properties of water at standard temperature and pressure [a]

Phase	μ / kG	α_μ / G/K	β_μ / µG/Pa
Ice	– 236.59	– 44.8	19.7
Liquid water	– 237.18	– 69.9	18.1
Water vapor	– 228.60	– 189	24465

a. Chemical potential μ, temperature coefficient α_μ and pressure coefficient β_μ.

Intensity of reactions. A feeling for the tendency to transform can be developed if we observe reactions of metals with sulphur. When we try to make magnesium, zinc, iron, copper, or gold react with sulphur, we observe a declining intensity of reaction. Magnesium and sulphur react explosively after initiation of the reaction, while gold hardly reacts at all. If other factors were equal, the different intensities of reactions might be taken as measures of different driving forces. We would have to conclude that the first of the reactions corresponds to the largest "drop" in Fig. 6.18. Assigning the initial elemental substances the same level of zero (this is indeed what is done in chemistry), MgS should have the lowest level of the reaction products in the list (Table 6.3).

Table 6.3: Chemical potential of some metal sulphides

Substance	MgS	ZnS	FeS	CuS	AuS
Chemical potential / kG	–347	–201	–100	–54	0

Phase changes. The condensation of water vapor, or the formation of ice out of water on a freezing day, are also examples of transformations. While we do not have a change of one chemical species into another here, we are clearly dealing with the transformation of one form of a substance into a distinctly different one. A similar case occurs when the yellow modification of mercuric iodide changes into its red version (the second reaction shown in Fig. 6.19). Returning to the phase changes of water, we would have to conclude that at room temperature, water has a lower chemical potential than ice, since the latter spontaneously changes into the former (Fig. 6.20). However, we know that the situation is reversed at lower temperatures: below the freezing point, liquid water spontaneously changes into solid water (ice). Values of the chemical potentials of water and ice (Table 6.2) confirm these interpretations.

$T = 298\text{K}$:

$$\underbrace{H_2O_{\text{solid}}}_{-236.59\,\text{kG}} \rightarrow \underbrace{H_2O_{\text{liquid}}}_{-237.18\,\text{kG}}$$

$T = 198\text{K}$:

$$\underbrace{H_2O_{\text{solid}}}_{-232\,\text{kG}} \leftarrow \underbrace{H_2O_{\text{liquid}}}_{-230\,\text{kG}}$$

Figure 6.20: H_2O changes its phase from one having a higher chemical potential at a particular temperature to a phase having a lower chemical potential.

6.4.4 Dependence of the Chemical Potential on Other Factors

Temperature dependence of the chemical potential. The observation that water turns into ice at low temperatures and ice melts at high temperatures leads us to a couple of conclusions. For one, the chemical potential of a substance depends upon its temperature (it depends upon many other factors as well). And secondly, there should be a temperature where the driving force of the transformation of ice to water or water to ice is zero: we know this as the melting point of ice. For temperature ranges that are not too great, the temperature dependence can be described by a linear approximation:

$$\mu(T, P_{ref}) = \mu(T_{ref}, P_{ref}) + \alpha_\mu \left(T - T_{ref}\right) \tag{6.24}$$

α_μ is the *temperature coefficient of the chemical potential*. It is listed in Table 6.2 for the chemical H_2O in its three phases. In Chapters 8 and 10, we will show that the temperature coefficient equals the *negative molar entropy* of the substance. This means that the chemical potential decreases with temperature. This may come as a surprise, considering that chemical transformations tend to become more vigorous if temperature increases. However, you have to remember that the quantity responsible for a reaction is the difference of chemical potentials for the reactants and the products; both sides of a reaction equation are influenced by a change of temperature.

If we now apply the idea of the chemical driving force as the reason for transformations and accept that the transformation between water and ice can go either way when the driving force is zero, we have a simple means of calculating the melting temperature by applying Equ.(6.24) to the two phases of H_2O (see Example 6.4). As stated before, the condition of vanishing chemical driving force is called *chemical equilibrium*.

Knowledge about the changes of chemical potentials with temperature can be applied to many interesting questions such as how iron can be obtained from iron oxide. At standard conditions (298 K), the reaction of iron oxide with carbon does not run spontaneously. If the temperature is raised, however, the chemical driving force changes and makes the reaction possible (see Example 6.8).

Pressure dependence of the chemical potential. At standard pressure of 1.013 bar, ice melts at 0°C and water vaporizes at 100°C. We know from experience, that these temperatures change if the pressure is increased or decreased. Increasing pressure makes ice melt at 0°C, meaning the melting point is lowered. In other words, chemical potentials must depend upon pressure. To apply this fact most easily, we can again use a linear approximation of the form

$$\mu(T_{ref},P) = \mu(T_{ref},P_{ref}) + \beta_\mu\left(P - P_{ref}\right) \tag{6.25}$$

Here, β_μ is the *pressure coefficient of the chemical potential*. Later in this chapter, we will see that the pressure coefficient is the molar volume of the substance. Using the combined knowledge of how pressure and temperature influence chemical potentials and applying the idea of vanishing chemical driving force for the altered condition of chemical equilibrium, we can calculate the change of melting point of ice as a consequence of pressure changes (see Example 6.5).

Dependence upon concentration. Clearly, chemical potentials of substances depend upon their concentration. This is most obvious in transport processes where substances diffuse, but it is equally visible in the transformation of α-glucose into β-glucose in the process called mutarotation (Fig. 6.3). The condition that changes during the reaction is the concentration of both substances and that leads to the changing speed. In the end, there is equilibrium for a particular ratio of concentrations of the substances involved in the reaction. For changes of concentration that are not too great, we can again use a linear approximation to the chemical potential:

$$\mu\left(T_{ref},P_{ref},c\right) = \mu\left(T_{ref},P_{ref},c_{ref}\right) + \gamma_\mu\left(c - c_{ref}\right) \tag{6.26}$$

Interestingly, the concentration coefficient of the chemical potential is the same for any dilute substance. It turns out to be $\gamma_\mu = 2.48\ \mathrm{G \cdot m^3/mole}$ (for standard conditions).

QUESTIONS

14. When toluene exists at equal concentrations in water and in air, in which of the environments does it have the higher chemical potential? Why? (See Fig. 6.2.)
15. Considering that the temperature coefficients of the chemical potential of substances are negative, how is it possible for a reaction that does not take place at room temperature to run spontaneously at higher temperatures?
16. Why should the driving force of a spontaneous chemical transformation be positive? Is there a similar rule for other processes, such as hydraulic or electric ones?
17. How is the concept of chemical equilibrium related to chemical potentials and chemical driving force?
18. What happens to the boiling point of water if air pressure is decreased? How can this be understood in terms of chemical potentials?
19. What is the role of energy in spontaneous transformations? In driven reactions? Give examples of non-spontaneous chemical change.

EXAMPLE 6.4. Melting point of ice.

Use the standard values of chemical potentials and temperature coefficients for water and ice—and the idea of chemical equilibrium—to find an approximation to the melting point of H_2O (values in Table 6.2).

SOLUTION: Since the transformation of water to ice or ice to water can go either way at the melting point, the chemical potential of the phases must be equal at that point:

$$\mu_{ice}\left(T_{melt}\right) = \mu_{water}\left(T_{melt}\right)$$

We express the chemical potentials of both substances in terms of standard potentials and the temperature coefficients (according to Equ.(6.24)):

$$\mu_{ice}^{0} + \alpha_{\mu,ice}\left(T_{melt} - T_0\right) = \mu_{water}^{0} + \alpha_{\mu,water}\left(T_{melt} - T_0\right)$$

Solving the equation and inserting values from Table 6.2 leads to a value of

$$\begin{aligned} T_{melt} &= \frac{\mu_{water}^{0} - \mu_{ice}^{0} + T_0\left(\alpha_{\mu,ice} - \alpha_{\mu,water}\right)}{\alpha_{\mu,ice} - \alpha_{\mu,water}} \\ &= \frac{-237180 - (-236590) + 298.15\left(-44.8 - (-69.9)\right)}{-44.8 - (-69.9)}\,\mathrm{K} = 274.6\,\mathrm{K} \end{aligned}$$

This is equal to about 1.5°C. Considering that this is just a linear approximation, the result is quite acceptable.

EXAMPLE 6.5. Changing the freezing point of water by changing the pressure.

Determine by how much the melting point of ice changes if the pressure is changed. Why does the melting temperature decrease with increasing pressure? Would this happen with any type of substance?

SOLUTION: Again, the chemical potentials of liquid and solid water have to be equal at the actual melting point, and again the potentials change with temperature, and this time also with pressure. Therefore, the following condition must be satisfied:

$$\begin{aligned} &\mu_{ice}^{0} + \alpha_{\mu,ice}\left(T - T_0\right) + \beta_{\mu,ice}\left(P - P_0\right) \\ &\qquad = \mu_{liquid}^{0} + \alpha_{\mu,liquid}\left(T - T_0\right) + \beta_{\mu,liquid}\left(P - P_0\right) \end{aligned}$$

For simplicity, take the value of the melting point T_f (at the reference pressure) as the reference temperature, in which case the reference potentials of ice and water are equal. With this in mind, we arrive at a relation between the change of pressure and temperature:

$$\frac{\Delta P}{\Delta T} = -\frac{\alpha_{\mu,liquid} - \alpha_{\mu,ice}}{\beta_{\mu,liquid} - \beta_{\mu,ice}}$$

Using the values for water from Table 6.2, we obtain the interesting result that the melting point of ice decreases with increasing pressure (with the corresponding values at 0°C we get the result of $\Delta P/\Delta T = -135$ bar/K). This is so because the pressure coefficient of ice is larger than that of water, a condition which holds only for water, and maybe one or two other substances.

Generally, however, the temperature of the melting point increases with increasing pressure. If the solid phase has a higher density, the molar volume and the pressure coefficient are smaller.

6.5 ENERGY IN CHEMICAL PROCESSES

The chemical potential of a species has been introduced as the tendency of a substance to change and has been compared to a level quantity such as gravitational potential or temperature. We know that potential differences are associated with the release or the use of quantities of energy; in other words, when a physical process takes place, the rate at which the fluidlike quantities go through a potential difference is related to the power of the process. This concept was introduced for graphically describing what happens in physical processes. We have studied the fall of water and the pumping of heat in terms of this image, and we will now do the same for processes involving chemical reactions.

6.5.1 Power of Chemical Processes and Energy Transfer

We can extract the fundamental aspects of energy in chemical processes from the foregoing discussion. When a substance flows from higher to lower chemical potential, energy is released (Fig. 6.21, left). Now consider a chemical reaction where substances disappear and appear. When a substance is consumed (Fig. 6.21, right), energy is released. We might be easily convinced of the validity of this idea if we look at nuclear reactions or the absorption of light. In such cases we are inclined to think that an object—a neutron, a nucleus, a photon—literally disappears. Since the object possessed energy, the energy it had must still be there, it must have been released. In the subatomic world, energy released is commonly involved in the creation of new objects, so energy is used as well.

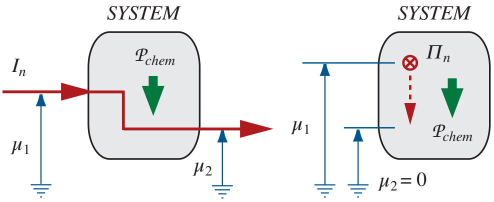

Figure 6.21: When a substance is flowing from higher to lower chemical potential, energy is released (left). If a substance is consumed in a chemical reaction, energy is released (right).

The rate at which energy is released is called *chemical power*. We can assume the power of a chemical process to follow the same basic rule that holds for fluid, electric, thermal, or mechanical phenomena. Therefore:

$$\mathcal{P}_{chem} = -\Delta\mu I_n \tag{6.27}$$

$$\mathcal{P}_{chem} = -\mu \Pi_n \tag{6.28}$$

The second expression requires a brief explanation. Here I consider the "unit process" of the disappearance or appearance of a substance without considering other substances that may be involved in a complete reaction. When a substance disappears—when it is literally destroyed—its energy is released. When a certain amount of a substance is created, it needs a well defined amount of energy. That is why the chemical potential is used in Equ.(6.28) in place of the a chemical potential difference. This case is well known to us from thermodynamics. When a unit of entropy is produced, a well defined amount of energy is needed. This is ensured by the fact that the temperature—the thermal potential—is absolute, i.e., it has an absolute zero point. So we expect the same to apply to the chemical potential. μ in Equ.(6.28) is the absolute value of the chemical potential of the substance being consumed or being created.

To complete the image of the role of energy in chemical processes, let us remember that chemical substances can be transported. When they enter (or leave) a system at a certain value of the chemical potential, there is an energy current associated with the transport (Fig. 6.22):

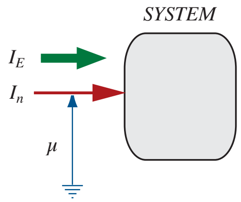

Figure 6.22: When a substance is transferred into or out of a system, energy is transferred as well.

$$I_{E,chem} = \mu I_n \tag{6.29}$$

This and the relations for power can be looked upon as giving us additional information concerning the nature of the chemical potential. If we have independent means for measuring the power of a chemical process and the conversion rate of amount of substance, chemical potentials can be determined.

6.5.2 Energy and the Driving Force of Chemical Reactions

Now we are in a position to answer the question of how to determine the chemical potential difference, i.e., the driving force, of a complete chemical reaction. Consider a chemical reaction involving several reactants (A_i) and several product substances (B_i) such as the one given in Equ.(6.18).

Each of the substances has its own chemical potential (dependent upon conditions). Figuratively speaking, the substances on one side of the reaction equation will be consumed, will disappear from this world, whereas the products will be literally produced. This means that energy is released equivalent to the amounts and the potentials of each disappearing substance, and energy is used according to the amounts and potentials of the substances being created.

The total power of the chemical reaction is the sum of all power terms calculated from each "unit process" according to Equ.(6.28). If we take the relation between reaction rates (Equ.(6.19)) into consideration and write the reaction equation with stoichiometric coefficients as in Equ.(6.18), we obtain:

$$\mathcal{P}_{Reaction} = \frac{1}{\nu_i}\left[\Delta\mu\right]_{Reaction} \Pi_{n,i} \tag{6.30}$$

with the term in brackets—the chemical potential difference—evaluated according to:

$$\left[\Delta\mu\right]_{Reaction} = \upsilon_1 \mu_{B1} + \upsilon_2 \mu_{B2} + \ldots - \left(\nu_1 \mu_{A1} + \nu_2 \mu_{A2} + \ldots\right) \tag{6.31}$$

It makes sense to accept this as the chemical potential difference pertaining to the reaction equation in Equ.(6.18). The *driving force* will be defined as the negative of the difference of chemical potentials of a transformation:

$$\mathcal{A}_R = -\left[\Delta\mu\right]_{Reaction} \tag{6.32}$$

There is an ambiguity in the value of the driving force for a complete chemical reaction. We could write the same reaction equation having stoichiometric coefficients multiplied by some factor, say two, which then doubles the potential difference. This ambiguity disappears when the driving force is used as in the computation of the power of a chemical process (see Equ.(6.30)).

6.5.3 Electrochemical Processes

In the following, electrochemical processes shall serve as an example for how to better understand the role of energy in chemical transformations. Technical applications range from batteries, accumulators, and fuel cells, to the production or the refining of metals in electrolysis. It might come as a surprise that the interaction of chemistry and electricity also applies to thermoelectric devices and solar cells.

An example of an electrochemical cell. Let me describe a particular electrochemical cell to show the details of reactions involved in such a device. We start with the observation that a rod of zinc will react (and apparently dissolve) in a solution of copper sulfate. At the same time, metallic copper will deposit upon the rod. Since we have Cu^{2+} ions in the solution, the reaction taking place can be described by the equation:

$$\underbrace{Zn + Cu^{2+}}_{(0+65.52)\,kG} \rightarrow \underbrace{Zn^{2+} + Cu}_{(-147.03+0)\,kG}$$

We will discuss the origin of values of chemical potential in Section 6.5.4. For now we take values from Table 6.4. In the given direction, the reaction is spontaneous. It involves moving two electrons from a zinc atom to a copper atom, but we do not notice this because of how the process proceeds. The net result of the reaction is the disappearance of the rod while some copper is deposited and entropy is produced.

If we wish to make use of the transfer of electrons in an electrical process, i.e., if the cell is to be turned into a battery, we somehow have to manage to separate the copper ions from the zinc rod and allow electrons to pass through an external wire (Fig. 6.23). This is accomplished in a cell with two compartments separated by a porous barrier. The barrier allows ions to pass but prevents any mixing of the solutions ($CuSO_4$ in the cathode compartment, $ZnSO_4$ in the anode compartment). Since the positive copper ions do not diffuse toward the positive zinc electrode, they are effectively confined to their compartment with the copper electrode. Now, in each part of the cell a separate reaction takes place:

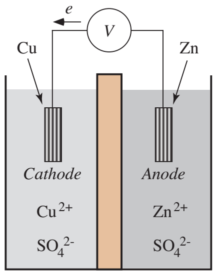

Figure 6.23: An electrochemical cell consisting of two compartments in which two reactions are taking place, each involving the exchange of electrons. The electrons are allowed to flow through an external wire.

$$\underbrace{Zn}_{0\,kG} \rightarrow \underbrace{Zn^{2+} + 2e}_{(-147.03+0)\,kG}$$

$$\underbrace{Cu^{2+} + 2e}_{(65.52+0)\,kG} \rightarrow \underbrace{Cu}_{0\,kG}$$

The transfer of charge is accomplished as desired: the electrons involved in the reaction pass from one compartment to the other through the external wire.

Electricity pumps and chemical pumps. Similar to other phenomena, electrochemical processes can be divided into two groups, namely one in which chemical reactions drive the flow of electricity, and another in which the flow of electricity is used to drive a chemical reaction that would not run by itself in this direction. From the viewpoint of the driven process, devices applying these phenomena might be called electricity pumps (Fig. 6.24) and chemical pumps (Fig. 6.25), respectively. In an electricity pump, electricity flows from a lower to a higher level, while in the chemical pump, substances are pumped from lower to higher chemical potentials.

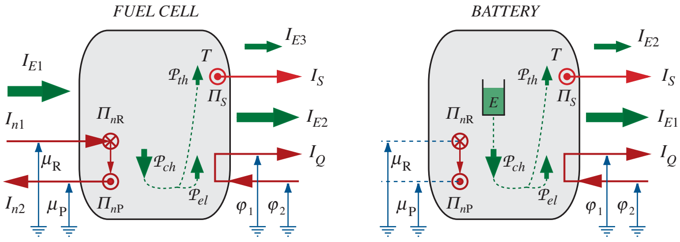

Figure 6.24: Chemical reactions drive the flow of electric charge in chemical electricity pumps. This requires energy which must be released in the chemical reactions taking place in the fuel cell (a) or the battery (b). The flow diagrams are those of irreversible processes. Some entropy is produced.

Examples of electricity pumps are fuel cells and the various forms of batteries. There is an important practical difference between fuel cells and batteries. In both, the substances undergo chemical reactions. In the former, the reactants are supplied continuously and the products are removed. In batteries, the chemicals are stored and then used up. This difference changes the form of the equations of balance used to describe each species, but it does not affect the principle of operation of the device.

In electrolysis and in the charging of rechargeable batteries, we simply let the processes just described run in the reverse direction: electric currents are used to drive a chemical reaction (see Fig. 6.25). The energy released in the fall of electric charge from higher to lower electric potential is used for the chemical transformation. Water can be split into hydrogen and oxygen; aluminum can be formed from its oxide; and copper can be refined. Reduction and oxidation reactions take place at the electrodes in the electrochemical cell. Electrolysis is often the only means of getting the reaction to proceed at all: the necessary transfer of electrons is forced by the electrical process.

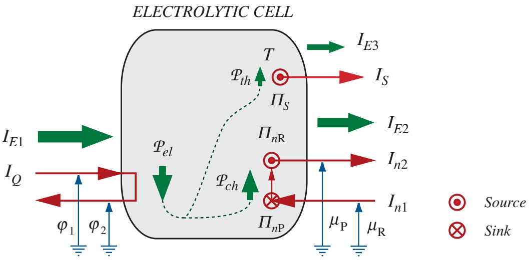

Figure 6.25: In an electrolytic cell, chemicals are changed by an electric current. Substances (such as water) enter the cell at a lower chemical potential and are destroyed, while new species (such as hydrogen and oxygen) are produced and leave the cell at a higher chemical potential. Note that some of the energy released by electricity is used to produce entropy.

6.5.4 Values of Chemical Potentials

If you consider the sheer endless numbers of chemical species, where each presents itself in different environments at different temperatures, pressures, concentrations, etc., you might get a feeling for the amount of work involved in getting the actual values of chemical potentials. Values are obtained by a multitude of methods used to measure various effects in chemical systems. Theory relates these measures to the one we finally want. A relatively simple example for what may be involved is the determination of the chemical potential of water from the voltage set up by a fuel cell converting hydrogen and oxygen (Example 6.6).

For now, we simply use the chemical potentials given to us in compilations created by researchers working in the field (see Table 6.4 for a few substances interesting to us in the examples and applications treated here). Let me discuss an interesting feature found in these tables, namely the fact that elemental substances in their most stable form are given potentials equal to 0 G.

The zero point of the chemical potential. The chemical potential is an absolute potential just like temperature and pressure, and unlike the potentials of gravity, motion, or electricity.[6] At conditions as they are found on earth, the chemical potential of a species is its mass (energy) divided by its amount of substance:

$$\mu \approx \frac{mc^2}{n} = M_0 c^2 \tag{6.33}$$

where c is the speed of light. This agrees with our knowledge of the relation of substances, potentials, and energy. The value $\mu_0 = M_0 c^2$ is the rest potential (for $T = 0$ K). Values for a few isotopes are presented in Table 6.1. They can be used for computing potential differences. These are so large that chemical driving forces of nuclear reactions are dominated by the rest potentials. Factors such as temperature and density play a role only under extreme conditions such as in some stellar interiors. This means that the chemical driving force of the decay of an isotope is more or less constant, a fact that leads to the well known exponential radioactive decay (remember the model in Section 6.2; see also Section 6.8).

Now, while this is simple and clear, it would be impossible to do calculations involving chemical reactions by using absolute values of the chemical potential; the differences occurring as the result of a reaction are so small that we would need figures with more than a dozen digits. Chemists have chosen a different approach: they arbitrarily set the chemical potential of the most stable form of the elemental substances equal to zero. The values of the chemical potentials of compounds therefore represent the difference between their own absolute values and those of the elements they are formed of; for this reason, the chemical potential reported in tables such as Table 6.4 is called the *chemical potential of formation* of a substance, and is denoted by μ_f^0, where f stands for formation, and the superscript 0 denotes standard conditions of temperature and pressure. This makes sense, because in a chemical reaction of compounds, the same elemental substances occur on either side of the equation. The reaction

$$\mathrm{CaC_2 + 2H_2O \;\rightarrow\; Ca(OH)_2 + C_2H_2}$$

may be understood as

$$\underbrace{\mathrm{CaC_2 + 2H_2O}}_{(-68+2(-237))\,\mathrm{kG}} \rightarrow \underbrace{\mathrm{Ca + 2C + 2H_2 + O_2}}_{0\,\mathrm{kG}}$$

$$\underbrace{\mathrm{Ca + 2C + 2H_2 + O_2}}_{0\,\mathrm{kG}} \rightarrow \underbrace{\mathrm{Ca(OH)_2 + C_2H_2}}_{(-897+209)\,\mathrm{kG}}$$

(values from Table 6.4). First, the reactants decay into their elements, then the products are formed out of these elements. Calculating the driving force of the reaction in this manner makes it unnecessary to use the absolute values of the potentials.

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[6] Obviously, potentials associated with non-conserved quantities (entropy and volume) are absolute. Gravitational and electric potentials and velocity and angular speed are related to the conserved quantities mass, charge, momentum, and angular momentum.

Table 6.4: Chemical potential of substances[a]

Formula	Substance	μ / kG[b]	α / G/K	β / μG/Pa
C (s)[c]	Carbon	0	– 5.69	5.4
C_2H_2 (g)	Ethyne	209.20	– 200.83	
CH_4 (g)	Methane	– 50.89	– 186.10	24465
CH_4O (l)	Methanol	– 166.35	– 126.74	
$C_6H_{12}O_6$ (aq)	Glucose	– 917.44		
C_7H_8	Toluene (g) Toluene (l)	122.39 110.61	– 319.70 – 219.00	
CO (g)	Carbon monoxide	– 137.15	– 197.56	
CO_2 (g) CO_2 (aq)	Carbon dioxide	– 394.40 – 385.99	– 213.68 – 113.00	24465
$CaCO_3$ (s)	Calcium carbonate	– 1128.76	– 92.88	36.92
CaC_2 (s)	Calcium carbide	– 67.78	– 70.29	28.9
$Ca(OH)_2$ (s)	Calcium hydroxide	– 896.76	– 76.15	33.2
Cl^- (aq)	Chlorine ion	– 131.26	– 56.48	18.0
Cu^{2+} (aq)	Copper ion	65.52	99.58	
Fe	Iron	0	– 27.32	7.1
Fe_2O_3	Iron oxide	– 743.58	– 87.4	30.4
H_2 (g)	Hydrogen	0	–131	24465
N_2 (g)	Nitrogen	0	– 191.50	24465
NH_3 (g)	Ammonia	–16.40	– 192.50	
Na^+ (aq)	Sodium ion	– 261.89	– 58.99	– 1.6
NaCl (s)	Table salt	– 384.03	– 72.13	27.02
O_2 (g) O_2 (aq)	Oxygen	0 16.44	– 205.02	24465
PbO_2 (s)	Lead dioxide	– 212.42	– 76.57	
$PbSO_4$ (s)	Lead sulfate	– 813.20	– 148.57	48.2
SO_4^{2-} (aq)	Sulfate ion	– 744.63	– 20.08	15.0
SiO_2 (s)	Silicon dioxide	– 856.48	– 41.46	22.6
Zn^{2+} (aq)	Zinc ion	– 147.03	112.13	– 26

a. G. Job: Chemische Potentiale ausgewählter Stoffe. www.job-stiftung.de.
b. At standard conditions: 298.15 K, 101,325 Pa, pure or 1 mole/L.
c. (s) solid, (l) liquid, (g) gaseous, (aq) aqueous

6.5.5 Entropy Production in Chemical Reactions

The energy released in chemical processes is often completely dissipated. Typical examples are the burning of fuels (Table 6.5 lists quantities of energy exchanged with entropy, i.e., in heating or cooling of the reacting fluid, called heating values). Entropy is produced at a rate that depends upon the power of the chemical process, and the temperature at which entropy production takes place (see Fig. 6.26). In the case of a chemical reaction, this leads to:

$$\Pi_S = \frac{1}{T}\frac{1}{\nu_i}\left[\Delta\mu\right]_{Reaction}\Pi_{n,i} \tag{6.34}$$

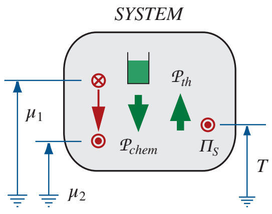

Figure 6.26: Entropy is produced in dissipative chemical processes. The diagram leaves an important question unanswered: what happens with the entropy that is produced?

Balance of entropy: Exothermic and endothermic reactions. Dissipation means that entropy has been produced. The consequence of a chemical reaction in a simple fluid is just that: all the energy released is used to produce entropy (see Fig. 6.26). What happens with the entropy produced?

Table 6.5: Heating Values of Fuels

Fuel	Formula	Higher[a] Heating Value[b] / kJ/kg
Carbon	C	32,800
Hydrogen	H_2	141,800
Methane	CH_4	55,530
Ethanol	C_2H_6O	29,670
Propane	C_3H_8	50,330
Gasoline	$C_nH_{1.87n}$	47,300
Natural Gas	$C_nH_{3.8n}N_{0.1n}$	50,000

[a] For liquid water in products (the Lower Heating Value is defined for gaseous water in products).

[b] Energy exchanged with entropy in cooling of the burning fluid.

The reacting fluid might simply store the new entropy which would often mean a rise of temperature. In order not to worry about the effect of changing temperatures, one normally calculates chemical driving forces and power or energy released by assuming that reactants and products are in the standard state. Under these circumstances, we would typically assume the entropy produced to be emitted together with an appropriate amount of energy: the reacting fluid undergoes cooling. Such a reaction is called *exothermic*.

The reasoning applied here leaves out an important aspect, namely, the change of entropy stored in the reacting system. Since the fluid is not the same chemically after the reaction has occurred, the entropy needed to maintain standard conditions of temperature and pressure will usually be different. As mentioned before, we can use the temperature coefficient of the chemical potential (Table 6.4) to infer the entropy of reactants and products. This allows us to calculate the change of entropy of the system as a consequence of the reactions.

In total, there are three possibilities (Fig. 6.27). Either, the change of entropy is *negative*, meaning, entropy comes out of storage. In this case, the entropy produced and the entropy from storage are emitted by the fluid. The reaction is *exothermic*. On the other hand, if the change of entropy of the fluid is *positive* (if entropy is needed for storage), there are two distinct cases. Either, the amount of entropy produced is more than enough to cover what has to be put in storage which means that the rest is emitted: the reaction is *exothermic*. Or, if the reaction does not produce enough entropy, the missing quantity must be taken from the environment: the fluid is heated and the reaction is said to be *endothermic*.

Exothermic reactions

(*Entropy is emitted*)

a. $\Delta S < 0 \quad \Rightarrow$

$$S_e = \Delta S - S_{prod} < 0$$

b. $\Delta S > 0 \;,\; S_{prod} > \Delta S \quad \Rightarrow$

$$S_e = \Delta S - S_{prod} < 0$$

Endothermic reactions

(*Entropy is absorbed*)

$$\Delta S > 0 \;,\; S_{prod} < \Delta S \quad \Rightarrow$$

$$S_e = \Delta S - S_{prod} > 0$$

Figure 6.27: Whether or not a chemical reaction is exothermic is decided by changes of the entropy of systems and the amount of entropy produced. These cases include the possibility of non-dissipative reactions ($S_{prod} = 0$).

Actually, the question of whether a reaction is exothermic or endothermic applies to non-dissipative reactions as well. No matter what happens, products are not the same as reactants. The entropy of the system will change, which either allows entropy to be emitted or to be absorbed from the environment. The environment, by the way, may very well be a liquid such as water in which dissolved substances react. In this case, the first effect of exothermic and endothermic reactions is an increase or decrease of the temperature of the solvent, respectively. Subsequently, entropy is exchanged with the wider environment.

6.5.6 Combined potentials

Substances are not only subject to chemical processes, they also undergo gravitational and electrical ones. This is so because they have mass and may be electrically charged. In flow processes, a substance may therefore be subject to more than one driving force at the same time. To conveniently describe flows in gravitational or electric fields, the gravitational and electric potentials are combined with the chemical potential of a species. Many processes may then be regarded as resulting from electrochemical or gravitochemical driving forces.

Electrochemical potential. The interaction of chemical and electrical processes is a widespread phenomenon. We know it from batteries and related technical devices and procedures, but it is just as important in biology. The nervous system and muscles of living beings crucially depends upon this interaction.

Imagine two regions separated by a membrane (Fig. 6.28). Assume the environments I and II to be different so that some dissolved substance “prefers” to be in II (this need not be the case in a biological application). As a result, we would expect the concentration of this substance to be higher in II than in I (remember the case of toluene in Fig. 6.2). As long as the equilibrium distribution has not been established, a chemical driving force “tugs” on the substance and makes sure that more of it ends up in environment II. Now, allow the substance to consist of ions, i.e., we assume it to be electrically charged. Having ions in solution sets up an electric field in the system. Therefore, there is an electric driving force “tugging” at the same particles. If the ions are positive and if we start with a distribution according to the purely chemical equilibrium (more of the stuff in environment II), there should be a tendency of the ions to drift from II to I, changing what used to be the chemical equilibrium, at the same time changing the electric field. In the end, we should expect a distribution of concentrations that makes the net driving force—the chemical and the electric effects—equal to zero: we have *electrochemical equilibrium*. The dissolved substance is in equilibrium if the concentrations are such that the difference of the *electrochemical potential* μ_{EC} across the membrane is zero:

$$\mu_{EC}(\mathrm{I}) = \mu_{EC}(\mathrm{II}) \tag{6.35}$$

This is only small part of the story of membrane potentials but it tells the important aspects we are interested in at this point. It tells us that when there are two forces present, it is the combined potential that determines processes and equilibria.

Energy considerations are a simple means for figuring out how to combine potentials. Energy is transferred when substances and charge flow, and the energy currents combine into a single one:

$$I_E = I_{E,chem} + I_{E,el} = \mu I_n + \varphi I_Q \tag{6.36}$$

The important point to note about combining potentials is the fact that substances and electric charge are directly coupled. Particles of a chemical species carry electric charge. Therefore, the electric current can be converted into an equivalent current of amount of substance. The current of amount of substance has to be multiplied by the molar charge (charge per amount of substance) to obtain the electric current. If e is the (positive) elementary charge, z the charge number of an ion, and N_0 is the number of particles per mole, we have

$$I_Q = zeN_0 I_n = z\mathcal{F} I_n \tag{6.37}$$

Remember that $\mathcal{F} = eN_0$ is called the Faraday constant ($\mathcal{F} = 96487$ C/mole). The last expression is introduced into Equ.(6.36), and the terms are combined. We see that the result can be expressed in terms of a combined *electrochemical potential*:

$$\mu_{EC} = \mu + z\mathcal{F}\varphi \tag{6.38}$$

If ions are flowing, we can consider differences of the electrochemical potential as the *combined driving force* acting upon a substance. Here, μ is the simple chemical potential as defined above.

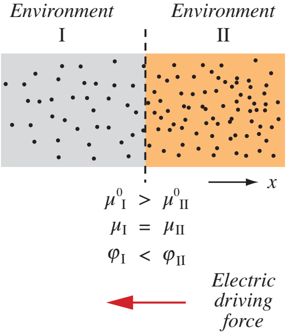

Figure 6.28: Two environments (I and II) and a dissolved substance. The standard chemical potential (i.e., for equal concentration) of the substance is higher in I than in II. The figure shows the condition of chemical equilibrium (higher concentration in II). If the particles are charged, there is an electric driving force for the particles from II to I. In final electrochemical equilibrium, the distribution of concentrations will be different.

Electrochemical reactions. In an electrochemical cell (such as a fuel cell or a battery), chemical reactions that run by themselves release energy which is used to drive an electric current through a voltage (Fig. 6.29). Put differently, a voltage is established by the chemical reactions. The processes are coupled just as they are in a flow of a charged species. A small integer number of units of charge are separated for every unit of chemical conversion in the reaction. If the process could proceed reversibly, the balance of power would lead to

$$0 = \frac{1}{\nu_1}[\Delta\mu]_{Reaction}\,\Pi_{\mathrm{A}1} - \Delta\varphi I_Q$$

If we use Equ.(6.37) and replace the current of substance by the (negative) conversion rate $\Pi_{\mathrm{A}1}$, we obtain

$$\frac{1}{\nu_1}[\Delta\mu]_{Reaction}\,\Pi_{\mathrm{A}1} = \Delta\varphi z\mathcal{F}(-\Pi_{\mathrm{A}1})$$

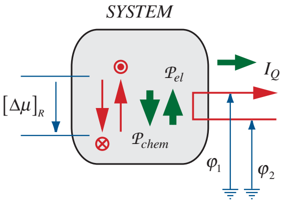

Figure 6.29: Process diagram of an electrochemical pump (a battery or similar device). Energy is released in a chemical reaction. The energy is used to drive an electric current.

or

$$\Delta\varphi = -\frac{1}{\nu_1 z \mathcal{F}}\left[\Delta\mu\right]_{Reaction} \tag{6.39}$$

$U = -\Delta\varphi$ is the open circuit voltage established by the cell. We have a relatively simple method here for determining chemical driving forces of reactions, or, alternatively, the means for predicting the performance of electrochemical cells from chemical data.

Gravito-chemical potential. When substances flow in the gravitational field, they are subject to two processes: chemical and gravitational. As in the case of charged substances in the electric field, there are two forces "tugging" on a substance at the same time, and phenomena are determined by a combined gravitochemical potential. The expression for the combined potential is derived analogously to what we did for the electrochemical potential. Therefore,

$$\mu_{GC} = \mu + M_0\varphi_G \tag{6.40}$$

is the gravito-chemical potential. μ is the standard chemical potential, $M_0 = m/n$ is the mass per amount of substance, i.e., the molar mass, and φ_G symbolizes the gravitational potential ($\varphi_G = gh$ in a field having constant g).

QUESTIONS

20. How can the destruction or production of a substance be used to argue that the chemical potential is an absolute quantity?
21. One mole of A plus two moles of B convert into one mole of C. How can Equ.(6.28) be used to argue that chemical potentials of the substances must be multiplied by the stoichiometric coefficients and then added up to yield the chemical driving force?
22. In a fuel cell, reactants are supplied and products are removed. How can the expression for the energy flows related to transports of substances be used to motivate the expression for the power of a chemical reaction?
23. What happens to the voltage of a battery when entropy is produced in the reactions? Does irreversibility affect the open circuit voltage of a battery?
24. What do the terms exothermic and endothermic mean?
25. Can a reversible chemical reaction be exothermic?
26. What must be the case if an endothermic reaction is to be excluded?
27. Under what conditions is it possible to define a combined potential for chemical and electrical effects?
28. How is the formula for the hydrostatic pressure in a liquid related to the expression for the gravitochemical potential?

EXAMPLE 6.6. The chemical potential of water determined from electric measurements.

At standard conditions, the voltage measured for an electrochemical cell (a fuel cell) converting hydrogen and oxygen to water has a maximum value of 1.23 V. Determine the chemical potential of water.

SOLUTION: We have to write down the reactions occurring at the electrodes of the fuel cell. H_2 is found to change into $2H^+$ and two electrons. At the other electrode, oxygen gas reacts with

H^+ ions and electrons to form water:

$$H_2 \rightarrow 2H^+ + 2e$$
$$2H^+ + 2e + \frac{1}{2}O_2 \rightarrow H_2O$$

This means that 2 moles of electrons are involved if 1 mole of hydrogen gas reacts. According to Equ.(6.39), the chemical potential of the reaction turns out to be

$$|\Delta\mu| = |z\mathcal{F}U_{el}| = 2 \cdot 96487 \cdot 1.23\,\mathrm{J/mole} = 237\,\mathrm{kG}$$

Since the chemical potentials of the hydrogen and oxygen gas are set equal to zero, this value also represents the chemical potential of water.

EXAMPLE 6.7. The voltage of a lead storage battery.

In a lead storage battery, an anode made out of lead and a cathode made out of lead dioxide are immersed in the same sulfuric acid solution. The reactions taking place at the electrodes are

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e$$
$$PbO_2 + 4H^+ + SO_4^{2-} + 2e \rightarrow PbSO_4 + 2H_2O$$

Calculate the voltage for each of the half reactions, and determine the voltage of the battery.

SOLUTION: The chemical potentials of the reactions can be taken from the previous tables:

$$\underbrace{Pb + SO_4^{2-}}_{(0+(-744.63))\mathrm{kG}} \rightarrow \underbrace{PbSO_4 + 2e}_{(-813.2+0)\mathrm{kG}}$$
$$\underbrace{PbO_2 + 4H^+ + SO_4^{2-} + 2e}_{(-212.4+4\cdot 0+(-744.63)+2\cdot 0)\mathrm{kG}} \rightarrow \underbrace{PbSO_4 + 2H_2O}_{(-813.2+2(-237.2))\mathrm{kG}}$$

The first reaction has a change of the chemical potential of – 68.6 kG corresponding to a voltage of 0.36 V (there are two electrons involved). For the second reaction, the figures are – 330.6 kG and 1.71 V, respectively. The voltage of the battery therefore is 2.07 V.

EXAMPLE 6.8. Obtaining iron from iron oxide.

Iron metal is obtained from the reaction of iron oxide, Fe_2O_3, with carbon, which yields iron and carbon monoxide. (a) Determine the reaction equation. (b) Calculate the minimal temperature for which the reaction spontaneously works.

SOLUTION: (a) To preserve the amount of substance of the elements involved, three moles of carbon must be combined with one mole of iron oxide:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

(b) At standard temperature and pressure, the reaction will not take place, as demonstrated by the values of the chemical potentials:

$$\underbrace{Fe_2O_3 + 3C}_{(-744+3\cdot 0)\mathrm{kG}} \rightarrow \underbrace{2Fe + 3CO}_{(2\cdot 0+3(-137))\mathrm{kG}}$$

If we want the reaction to proceed, the chemical potential on the left must be larger than that on the right-hand side of the equation. Since the chemical potential can be changed by changing the temperature, we have to look for that particular temperature for which the chemical potentials of the reactants and the products are equal:

$$\mu_{f,1}^{0}+\alpha_{\mu,1}\left(T-T_0\right)+3\left(\mu_{f,2}^{0}+\alpha_{\mu,2}\left(T-T_0\right)\right)=$$
$$2\left(\mu_{f,3}^{0}+\alpha_{\mu,3}\left(T-T_0\right)\right)+3\left(\mu_{f,4}^{0}+\alpha_{\mu,4}\left(T-T_0\right)\right)$$

for a general reaction. The numerical values are taken from Table 6.4:

$$-744\cdot 10^3-87.4\Delta T+3\cdot\left(0-5.69\Delta T\right)=2\cdot\left(0-27.3\Delta T\right)+3\cdot\left(-137\cdot 10^3-197.5\Delta T\right)$$

from which we determine ΔT to be 614 K. In this linear approximation, we expect iron to be formed at temperatures above 640°C. Even though the temperature coefficients depend quite strongly upon temperature, the approximation is useful as a first guess for several hundreds of degrees above the reference value. This is so because changes of the coefficients are affected similarly by changes of temperature on both sides of the reaction equation.

EXAMPLE 6.9. Entropy produced and exchanged in the reaction of H_2 and O_2.

(a) Consider the reaction which forms water out of hydrogen and oxygen. How much entropy is produced in forming one mole of water? (b) Does the product contain more entropy than the reactants? (c) Is the reaction exothermic or endothermic? How much entropy and energy are exchanged in heating or cooling? Remember that the reaction is assumed to proceed at constant temperature and pressure.

SOLUTION: (a) The amount of entropy produced is equal to the energy dissipated, divided by the temperature of the fluid. We have

$$\bar{s}_{prod}=-\frac{1}{T}\left[\mu_{\mathrm{H_2O}}-\left(\mu_{\mathrm{H_2}}+0.5\mu_{\mathrm{O_2}}\right)\right]$$
$$=-\frac{1}{298}\left[-237.2\cdot 10^3-\left(1\cdot 0+0.5\cdot 0\right)\right]\frac{\mathrm{J}}{\mathrm{K\cdot mole}}=796\frac{\mathrm{J}}{\mathrm{K\cdot mole}}$$

(b) We need to know the molar entropies of the species involved. The change of entropy of the substances calculated for the reaction is

$$\Delta\bar{s}=\bar{s}_{\mathrm{H_2O}}-\left(\bar{s}_{\mathrm{H_2}}+0.5\bar{s}_{\mathrm{O_2}}\right)$$
$$=69.9\frac{\mathrm{J}}{\mathrm{K\cdot mole}}-\left(1\cdot 130.6+0.5\cdot 205\right)\frac{\mathrm{J}}{\mathrm{K\cdot mole}}=-163.2\frac{\mathrm{J}}{\mathrm{K\cdot mole}}$$

This means that water contains less entropy than the elemental substances out of which it is formed.

(c) Considering that entropy has been produced and that the entropy content has decreased, it is clear that the fluids must be cooled. The amount of entropy exchanged is given by

$$\bar{s}_e=\Delta\bar{s}-\bar{s}_{prod}=-163.2\frac{\mathrm{J}}{\mathrm{K\cdot mole}}-796\frac{\mathrm{J}}{\mathrm{K\cdot mole}}=-959\frac{\mathrm{J}}{\mathrm{K\cdot mole}}$$

This value, multiplied by the temperature of the fluid, is equal to the energy emitted ($\bar{e}_{th}$):

$$\bar{e}_{th}=T\,\bar{s}_e=298\,\mathrm{K}\cdot\left(-959\frac{\mathrm{J}}{\mathrm{K\cdot mole}}\right)=-285.8\cdot 10^3\frac{\mathrm{J}}{\mathrm{mole}}$$

This should be equal to the heating value reported in tables of fuels (see Table 6.5). We have calculated the energy exchanged in cooling of the system for one mole of H_2 gas. To obtain the same number for a kilogram of H_2, we divide by the molar mass of the gas and obtain a value of $285.8 \cdot 10^3$ kJ/mole / 0.0020 kg/mole = 143 MJ/kg.

6.6 INCOMPRESSIBLE FLUIDS, IDEAL GASES, AND DILUTE SOLUTIONS

In subsequent sections, we will deal with some concrete chemical processes. The types of systems involved in these transformations are liquids, perfect gases and liquids with small amounts of impurities dissolved in them. To prepare later applications, we will take a look at their properties from a chemical perspective.

6.6.1 Incompressible Fluids

What we need to know about *incompressible fluids* is summarized by observing that the pressure of the fluid does not depend upon the temperature. In other words, pressure and temperature can be changed independently. Since transports of substances depend upon pressure differences, temperature does not enter as a direct factor.

As mentioned before, since flows are determined by chemical potential differences, the chemical potential of an incompressible fluid is expected to depend directly upon its pressure. To derive the relation, we can make use of what we know about liquids at rest in the gravitational field of the Earth, such as water in a lake. Consider a column of liquid above a surface in a field of strength g (Fig. 6.30). We know that the pressure of the liquid increases linearly in the negative h-direction (see Chapter 1):

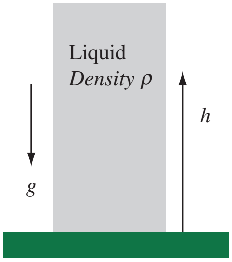

Figure 6.30: An incompressible liquid in a gravitational field. The fluid is assumed to be at rest.

$$P - P_0 = -\rho g\left(h - h_0\right) \tag{6.41}$$

The index 0 refers to a reference point in the fluid. Now we apply the concept of the gravito-chemical potential (Section 6.5.6) to the fluid at rest. While the gravitational potential decreases downward (in the negative h-direction), the (intrinsic) chemical potential of the fluid increases. This is so because the pressure increases downward which means that if there were no other influence, the fluid should flow upward by itself (in the direction of decreasing pressure). The fluid is at rest, leading us to conclude that the combined potentials, i.e., the gravito-chemical potential μ_{GC} is constant in the vertical direction:

$$\mu + M_0 gh = \mu_0 + M_0 gh_0 \tag{6.42}$$

If we now combine the last two equations, we can derive the relation between the chemical potential of the liquid and its pressure:

$$\mu = \mu_0 + \bar{v}\left(P - P_0\right) \tag{6.43}$$

where $\bar{v}$ is the molar volume of the incompressible fluid (Equ.(6.9)).

6.6.2 The Ideal Gas

The model of the *ideal gas* has been discussed at length in Chapter 5 where we derived thermal relations applying to this model substance. The relation between pressure, volume, and temperature of an ideal gas is

$$PV = RnT \tag{6.44}$$

The universal gas constant, has a value of $R = 8.31441$ J/(mole·K). n measures the amount of substance of the gas. For our future discussions, it is important to remember that this model agrees well with reality for dilute gases, meaning density and pressure should be low. Only if the temperature is very high, can relatively dense fluids remain in the state of the ideal gas. For example, the interior of the Sun satisfies this condition where the density is more than 100 times the standard density of water.

As in the case of incompressible liquids, we shall use the idea of the gravitochemical potential of an ideal gas in a gravitational field to derive the dependence of the chemical potential upon pressure. Since the gas is compressible, there are two independent variables to consider, such as pressure and temperature. Since we are interested in the relation between the chemical potential and pressure, we shall take the temperature as constant. In other words, we are going to derive the *pressure dependence of the ideal gas at constant temperature*. Consider a column of ideal gas above a surface in a field of strength g (Fig. 6.30, this time with variable density). The discussion of an isothermal atmosphere in a constant-g field (see Problem 7 in Chapter 5) yielded the following pressure-height relation:

$$\ln\left(P/P_0\right) = -\frac{M_0 g}{RT}\left(h - h_0\right) \tag{6.45}$$

The index 0 refers to a reference level. The condition of constant gravito-chemical potential (Equ.(6.42)) still holds. Combining this and the last equation leads to

$$\mu = \mu_0 + RT \ln\left(\frac{P}{P_0}\right) \tag{6.46}$$

for the *chemical potential of an ideal gas at constant temperature*. This will be used presently to derive the important properties of components of mixtures of gases and dilute solutions.

6.6.3 Mixtures of Ideal Gases

Many substances are mixtures of pure components, which were the focus of most of what we have discussed so far. In general, mixing pure substances leads to a variety of new effects. However, in this section, we will study only the simplest type of mixture, namely that of ideal gases. Such mixtures do not furnish a lot of new physics; still, they allow us to introduce concepts which are useful in applications.

The molar fraction. Our first task is to describe the composition of a mixture made up of different substances. Each of the N component furnishes a certain amount of substance n_i toward the total amount:

$$n = \sum_{i=1}^{N} n_i \tag{6.47}$$

The relative amount

$$\bar{x}_i = n_i / n \tag{6.48}$$

is called the *mole fraction* of component *i* (this is a generalization of Equ.(6.12)). Naturally, the mole fractions of all the parts together add up to 1. If the composition of a mixture is known in terms of its mole fractions, the average or apparent molar mass M_0 may be calculated based on molar masses of the individual components M_{0i}. The molar mass of the mixture is equal to the ratio of its mass to its total amount of substance. Replacing the total mass by the sum of the masses of each component leads to

$$M_0 = \sum_{i=1}^{N} \bar{x}_i M_{0i} \tag{6.49}$$

In Chapter 5, we used this concept in simple contexts. Air at low densities or the gas at the center of the Sun furnish good examples of mixtures of ideal gases.

Partial pressure of a component of a mixture. Consider a mixture such as air (see Table 6.6). The interesting point about it is that it behaves just like a pure ideal gas. If we describe this "pure" substance by its apparent molar mass, we can treat it as if it were made up of pure helium or any other pure substance, for that matter. In other words, the mixture of ideal gases is an ideal gas itself. If we write the equation of state of the ideal gas for this substance expressed in terms of the amounts of substance of the components, we obtain

$$PV = nRT = \left(\sum_{i=1}^{N} n_i \right) RT \tag{6.50}$$

Using the mole fraction, the right-hand side of this equation can be written in the following form:

$$nRT = \left(\sum_{i=1}^{N} \bar{x}_i \right) nRT = \left(\sum_{i=1}^{N} \bar{x}_i \right) PV = \left(\sum_{i=1}^{N} \bar{x}_i P \right) V \tag{6.51}$$

We now call the term

$$P_i = \bar{x}_i P \tag{6.52}$$

the *partial pressure* of component *i*, and we see that the sum of the partial pressures is the total pressure of the mixture:

$$P = \sum_{i=1}^{N} P_i \tag{6.53}$$

There is a simple interpretation to these equations. In a mixture of ideal gases, each component exists as if it were completely independent of the others, filling the total volume *V* at the temperature *T* of the mixture. Each component then contributes its share P_i to the total pressure. Also, each part of the mixture obeys the equation of state of the ideal gas:

$$P_i V = n_i RT \tag{6.54}$$

Remember that these formulas hold only for mixtures of ideal gases. If components of a mixture interact, they cannot be considered independent of each other, which leads to effects not described by this model.

Table 6.6: Composition of dry air

Component	**Mole fraction**	**Molar mass /** kg/mole
Nitrogen	0.7808	0.02802
Oxygen	0.2095	0.0320
Argon	0.0093	0.03994
Carbon dioxide	0.0003	0.04401
Others	0.0001	

Molar entropy and energy. For thermodynamic purposes, we need to know such quantities as the entropy and the energy of a body. In the case of mixtures it might be necessary to compute these properties from those of the components.

Since, in our model, the components are independent of each other, each has its entropy and energy. Considering that these quantities are additive properties of a system, the total entropy or energy must be the sum of the parts:

$$S = \sum_{i=1}^{N} S_i \quad , \quad E = \sum_{i=1}^{N} E_i \tag{6.55}$$

These equations can be written in terms of the molar quantities

$$n\bar{s} = \sum_{i=1}^{N} n_i \bar{s}_i \quad , \quad n\bar{e} = \sum_{i=1}^{N} n_i \bar{e}_i \tag{6.56}$$

Divided by the total amount of substance, they take the form

$$\bar{s} = \sum_{i=1}^{N} \bar{x}_i \bar{s}_i \quad , \quad \bar{e} = \sum_{i=1}^{N} \bar{x}_i \bar{e}_i \tag{6.57}$$

This means that the molar entropy and the molar energy of the mixture are given in terms of the mole fractions and the molar entropy and energy of the components. The latter quantities have to be evaluated at the conditions (P and T) of the mixture.

Chemical potential of a component. A component i in a mixture at total pressure P and temperature T has a (partial) pressure P_i (see Equ.(6.52)) and the same temperature T as the mixture. Therefore, according to Equ.(6.46), its chemical potential is

$$\mu_i = \mu_{i,0} + RT \ln\left(\frac{P_i}{P_0}\right) = \mu_{i,0} + RT \ln\left(\frac{\bar{x}_i P_0}{P_0}\right)$$

i.e.,

$$\mu_i = \mu_{i,0} + RT \ln\left(\bar{x}_i\right) \tag{6.58}$$

Spatially separated components and mixing. At first sight it appears as if mixtures of ideal gases could be described in an alternative but equivalent manner. The equation of state of the ideal gas suggests that we can consider the mixture to be made up of spatially separate components (each with its amount of substance n_i), all at the same pressure and temperature (Fig. 6.31b). Each component would then occupy a partial volume V_i, and the sum of these would be the total volume V.

It is true that you get equivalent results for all quantities calculated above where we considered each component to occupy the total volume at some partial pressure, except for one: the entropy of the mixture is not equal to the sum of the entropies of the spatially separate components. Therefore, the two situations are by no means equivalent. We can see the difference easily in qualitative terms: if we were to remove the wall separating the two gases in Fig. 6.31b, both would diffuse and finally occupy the entire volume as in Fig. 6.31a. Since diffusion is dissipative, entropy must have been produced.

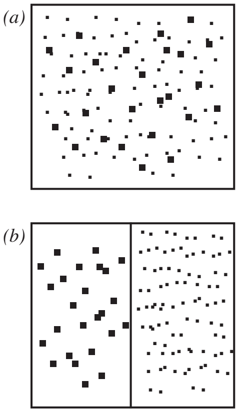

Figure 6.31: The cases of two different substances being spatially separate and mixed, are not equivalent. If the separating wall is removed, the gases diffuse and entropy is produced.

A quantitative analysis supports this view. The entropy of the system made up of the two separate ideal gases is calculated according to

$$\begin{aligned} S = S_A + S_B = S_{A0} + n_A \bar{c}_{PA} \ln\left(\frac{T}{T_0}\right) - n_A R \ln\left(\frac{P}{P_0}\right) \\ + S_{B0} + n_B \bar{c}_{PB} \ln\left(\frac{T}{T_0}\right) - n_B R \ln\left(\frac{P}{P_0}\right) \end{aligned}$$

The entropy of the mixture, on the other hand, is equal to

$$\begin{aligned} S_2 = S_A + S_B = S_{A0} + n_A \bar{c}_{PA} \ln\left(\frac{T}{T_0}\right) - n_A R \ln\left(\frac{P_A}{P_0}\right) \\ + S_{B0} + n_B \bar{c}_{PB} \ln\left(\frac{T}{T_0}\right) - n_B R \ln\left(\frac{P_B}{P_0}\right) \end{aligned}$$

where P_A and P_B are the partial pressures of the two components. The difference in entropy between the two cases is given by

$$\begin{aligned} S_2 - S_1 &= -\left\{ n_A R \ln\left(\frac{P_A}{P}\right) + n_B R \ln\left(\frac{P_B}{P}\right) \right\} \\ &= -n\left\{ \bar{x}_A R \ln\left(\bar{x}_A\right) + \bar{x}_B R \ln\left(\bar{x}_B\right) \right\} \end{aligned} \tag{6.59}$$

The x_i are the mole fractions of the parts of the mixture. Since these quantities are less than 1, the quantity calculated in Equ.(6.59) is positive: entropy has been produced.

There seems to exist a paradoxical situation. If the two components in Fig. 6.31 are identical, we know that nothing happens upon removal of the wall. On the other hand, Equ.(6.59) suggests that entropy must be produced even in this case. Since this is obviously not so, we have to explain the difference between "identical" and "different" substances. The amount of entropy produced is independent of how "different" the two components are, so there cannot be a gradual change between the two situations.

Either the gases are identical, or they are not, however slight their difference might be. The gases must notice the difference in the environment into which they are diffusing in the case of initially separate parts. If the substances are identical, there is no different environment, and there is no diffusion.

This phenomenon is called Gibbs' paradox. It calls for a quantum view of matter: there cannot be a gradual change of substances from "identical" to "different."

6.6.4 Dilute Solutions

If they are dissolved in fluids, substances can be made to behave according to the model of the ideal gas. As long as the *concentration* (Equ.(6.14)) of the solute is small enough, it has a pressure which is related to the Kelvin temperature by the law

$$P_s = RT\,\bar{c}_s \tag{6.60}$$

This relation is equivalent to the ideal gas law if the constant R in it takes the same value as the universal gas constant. Experiments tell us that this is the case. Most interestingly, it does not matter what type of stuff is dissolved; it may be a salt, or a substance composed of macromolecules, or even of macroscopic particles. Measurement of the pressure of the dissolved substance yields its concentration, from which we can compute the amount of substance dissolved.

In Section 6.1 we discussed that in order to understand phenomena such as osmosis, we have to assume that the solute decreases the pressure of the solvent:

$$P_f = P_{f,0} - P_s \tag{6.61}$$

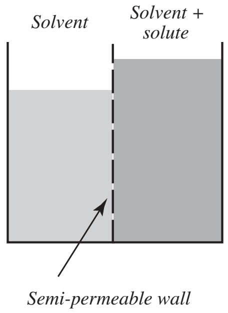

Figure 6.32: Osmosis occurs if two cells, one with only a solvent (water), the other with the solvent and a solute (sugar), communicate through a membrane which lets only the solvent pass. The solution draws more water which causes the fluid level to rise.

$P_{f,0}$ represents the pressure of the pure solvent (liquid without any solutes). Now we know how to understand this. The solvent naturally has a pressure of its own. The dissolved substance, i.e., the "gas" inside the solvent, has a pressure according to Equ.(6.60) which adds to the pressure of the liquid (the solvent). The total pressure of the solution is therefore the sum of the pressures of the solvent and of the solute. Since the total pressure is made up of several contributions, the terms P_f and P_s of Equ.(6.61) are called *partial pressures*.

One way of observing the influence of a solute on the solvent is through the phenomenon of *osmosis*. If a cell containing a solution is separated from the pure solvent by a semipermeable membrane (permeable only to the solvent), more of the solvent is literally drawn into the cell to dilute the solution. As a result, the level of the fluid in a cell containing solvent and solute (as in Fig. 6.32) rises above the level in the other cell. The difference of the pressures of the fluids indicated by the respective levels is called the *osmotic pressure* of the solute.

While osmosis is easily observed, it does not lend itself that easily to precise measurements. Usually, the effect of the pressure of the solute is observed indirectly in that it decreases the vapor pressure of the solvent. The change of vapor pressure, in turn, increases the temperature of vaporization and decreases the melting point. Measuring the latter effect is an important method of determining the molar mass of a dissolved substance.

Chemical potential of solute. The solute of a solution is like an ideal gas; it behaves like a gas all by itself with a vacuum as its "solvent." Therefore we can treat it just like an ideal gas in empty space, which means that its chemical potential must obey the relation

$$\mu_s(T,\bar{c}) = \mu_s(T,\bar{c}_0) + RT \ln\left(\frac{\bar{c}}{\bar{c}_0}\right) \tag{6.62}$$

Since at constant temperature, concentration and pressure are proportional, this result is equivalent to what was derived in Equ.(6.46). Note that this relation applies as well to substances dissolved in gels or solids which is important when we want to understand diffusion of substances through matter at rest.

Chemical potential of solvent. We treat the solvent as an incompressible fluid (liquid) which means that, according to Equ.(6.43), the chemical potential difference for the solvent with and without solute must be

$$\mu_f(T,P_f) - \mu_f(T,P_{f,0}) = \bar{v}_f\left(P_f - P_{f,0}\right)$$

Since the difference of solvent pressures is due to the solute (Equ.(6.61)), we have

$$\mu_f(T,P_f) - \mu_f(T,P_{f,0}) = -\bar{v}_f P_s \tag{6.63}$$

for the chemical potential of the solvent in a solution. It is customary to introduce the mole fraction of the solute in this equation. Since the amount of the substance dissolved is taken to be small compared to the amount of substance of the solvent, this quantity is nearly equal to

$$\bar{x}_s = n_s \big/ \left(n_f + n_s\right) \approx n_s / n_f$$

Together with Equ.(6.60), we arrive at the final result

$$\mu_f(T,P_f) = \mu_f(T,P_{f,0}) - RT\,\bar{x}_s \tag{6.64}$$

for the dependence of the chemical potential of the solvent on the amount of substance dissolved in it. This is what we need to get quantitative results for *osmosis* and other effects such as changes of vapor pressure and changes of boiling and melting points. This expression is equivalent to the one used for the flow of water into dried lentils in the dynamical model formulated in Section 6.7.4.

6.6.5 Pressure and Temperature Dependence of Chemical Potentials

As we have seen, chemical potentials of substances depend upon many factors. Concentration of dilute substances was discussed in previous subsections. Here, I will discuss the relation of the pressure and temperature coefficients (Section 6.4.4) with volume and entropy of a substance. The treatment will be informal; formal derivations can be found in Chapters 8 (Section 8.4.1) and 10.

Pressure dependence of the chemical potential. Take a look at what the special results previously derived suggest to us. The chemical potential of an incompressible fluid depends only upon pressure (Equ.(6.43)) so it is easy to see how it depends upon this variable. Equ.(6.43) tells us that the pressure coefficient $\beta_\mu = \Delta\mu/\Delta P$ of the chemical potential, i.e., the factor shows how the chemical potential changes with pressure, is the molar volume of the fluid:

$$\beta_\mu = \bar{v} \tag{6.65}$$

We can use the pressure dependence of the chemical potential of the ideal gas to derive this relation equally well. This result is correct in general for fluid systems as we will see in Chapter 10. In other words, the chemical potential of a fluid increases with pressure if everything else stays constant (Fig. 6.33).

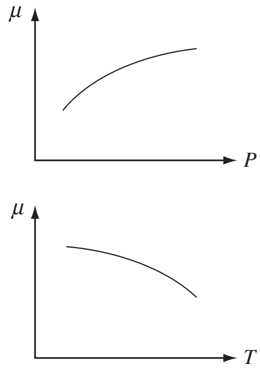

Figure 6.33: Chemical potential of a fluid as a function of pressure (top) and temperature (bottom).

Temperature dependence of the chemical potential. Imagine a fluid going through a chemical and thermal potential difference. The energy released can be expressed as $\Delta\mu I_n + \Delta T I_S$. If the current of entropy is coupled to the current of amount of substance, this form suggests a relation between the temperature change of the chemical potential and the entropy per amount of substance:

$$\alpha_\mu = -\bar{s} \tag{6.66}$$

Naturally, this is no more than a suggestion, but it can be proved for fluids that the temperature coefficient α_μ is indeed equal to the negative molar entropy (entropy per amount of substance) of the substance. Some temperature coefficients of the chemical potential are listed in Table 6.4. Contrary to the case of pressure, the chemical potential decreases with temperature (Fig. 6.33).

QUESTIONS

29. Why does a doubling of the pressure of a gas or the concentration of a dissolved substance always increase the chemical potential by the same value, independent of the initial values of pressure or of concentration?
30. When air and water are in contact and the air contains carbon dioxide, some of the CO_2 will go into the water. Why? How can we use the idea of chemical potentials and the chemical driving force to calculate how much CO_2 will end up in the water? What information do we need to perform this calculation?
31. What does the partial pressure of a component of a mixture of ideal gases depend upon?
32. Why is entropy produced when two different gases (originally at the same temperature and pressure) are mixed?
33. What effect does dissolving a substance in a liquid have upon the liquid? What does the effect have to do with chemical potentials and pressures?
34. Dissolving one mole of table salt in water leads to twice the osmotic effect compared to when we dissolve one mole of sugar. Why?
35. Why does the temperature of vaporization of a liquid go up when a substance is dissolved in it? Why is the effect of equal amounts of substance of salt or sugar different?

EXAMPLE 6.10. The temperature coefficients of energy and enthalpy of a mixture.

Show that the molar temperature coefficients of energy and of enthalpy (the specific heats) of a mixture can be calculated as the sum of the products of molar fractions and the coefficients for each component. Also, give the formulas for the entropy capacities of the mixture.

SOLUTION: The temperature coefficient of energy is the derivative of the energy with respect to temperature. Applying this definition to Equ.(6.57)$_2$ yields

$$\bar{c}_V = \frac{d\bar{e}}{dT} = \frac{d}{dT}\sum_{i=1}^{N}\bar{x}_i\bar{e}_i = \sum_{i=1}^{N}\bar{x}_i\frac{d}{dT}\bar{e}_i = \sum_{i=1}^{N}\bar{x}_i\bar{c}_{Vi}$$

The molar temperature coefficient of enthalpy of the ideal gas is defined as the derivative of the enthalpy with respect to temperature. We first have to show that the molar enthalpy can be calculated similarly to Equ.(6.57):

$$n\bar{h} = E + PV = \sum_{i=1}^{N}E_i + \left(\sum_{i=1}^{N}P_i\right)V = \sum_{i=1}^{N}\left(E_i + P_iV\right) = \sum_{i=1}^{N}n_i\left(\bar{e}_i + P_i\bar{v}_i\right) = \sum_{i=1}^{N}n_i\bar{h}_i$$

Therefore, the derivative of the molar enthalpy of the mixture is equal to

$$\bar{c}_P = \sum_{i=1}^{N}\bar{x}_i\bar{c}_{Pi}$$

The entropy capacitances are related to the temperature coefficients through the temperature of the mixture. Since every component has the same temperature, the equations just derived apply to the entropy as well:

$$\bar{\kappa}_P = \sum_{i=1}^{N}\bar{x}_i\bar{\kappa}_{Pi}$$

The equation holds also for the entropy capacitance at constant volume.

Table 6.7: Mass fractions of the components of dry air

Component	n_i / mole	M_{0i} / kg/mole	m_i / kg	**Mass fraction**
N_2	0.7808	0.02802	0.0219	0.756
O_2	0.2095	0.0320	0.0067	0.231
Ar	0.0093	0.03994	0.00037	0.0128
CO_2	0.0003	0.04401	0.000013	0.00045
	1.0		0.02897	1.0

EXAMPLE 6.11. The molar mass of air and mass fractions of the components.

Air at standard conditions can be considered to be a mixture of ideal gases. The mole fractions of the major components of dry air are given in Table 6.6. (a) Calculate the apparent molar mass of dry air. (b) Calculate the mass fraction of each of the components.

SOLUTION: (a) The average or apparent molar mass is computed according to Equ.(6.49):

$$\begin{aligned} M_0 &= \sum_{i=1}^{N}\bar{x}_iM_{0i} \\ &\approx (0.781\cdot 0.028 + 0.2095\cdot 0.032 + 0.0093\cdot 0.0399 + 0.0003\cdot 0.044)\,\text{kg/mole} \\ &= 0.0290\,\text{kg/mole} \end{aligned}$$

(b) The mass of each component is calculated using the amount of substance and the molar mass. Giving each component an amount of substance equal to the mole fraction makes the total amount of substance 1 mole. The results appear in Table 6.7.

Note that the difference between the molar fraction and the mass fraction is small if the molar mass of the component is similar to the apparent molar mass of the mixture. This holds for nitrogen and for oxygen.

EXAMPLE 6.12. Temperature coefficients of energy and enthalpy of a mixture.

Take a sample of dry air at a temperature of 300 K and a pressure of 0.90 bar. (a) Calculate the partial pressures of nitrogen, oxygen, and argon. (b) Calculate the molar temperature coefficients of energy and of enthalpy of these components and of the air sample as a whole.

SOLUTION: (a) With the total pressure known, the partial pressures of different components are calculated easily using the mole fractions according to Equ.(6.52). The mole fractions of the three most abundant components are given in Table 6.8 of Example 6.11. With these values we obtain

$$P_{N_2} = \bar{x}_{N_2} P = 0.781 \cdot 9 \cdot 10^4 \,\text{Pa} = 7.03 \cdot 10^4 \,\text{Pa}$$

$$P_{O_2} = \bar{x}_{O_2} P = 0.2095 \cdot 9 \cdot 10^4 \,\text{Pa} = 1.89 \cdot 10^4 \,\text{Pa}$$

$$P_{Ar} = \bar{x}_{Ar} P = 0.0093 \cdot 9 \cdot 10^4 \,\text{Pa} = 837 \,\text{Pa}$$

(b) Table 6.8 displays our results. The molar temperature coefficients of energy and of enthalpy of the ideal gas are computed according to the results of Example 6.10. The values of the molar temperature coefficient of energy can be read from Fig. 5.14 in Chapter 5. The temperature coefficients of enthalpy are obtained by adding the value of the universal gas constant.

Table 6.8: Temperature coefficients of energy and of enthalpy of dry air

Component	Mole fraction	c_V / J/(K·mole)	c_p / J/(K·mole)
nitrogen	0.7808	20.9	29.2
oxygen	0.2095	21.2	29.5
argon	0.0093	12.5	20.8

Neglecting other components, we get values of 20.88 J/(K·mole) and 29.17 J/(K·mole) for the temperature coefficients of energy and of enthalpy for the mixture. This is very nearly the value obtained for nitrogen alone.

EXAMPLE 6.13. Entropy produced in mixing two ideal gases.

(a) Calculate the amount of entropy produced if two different gases of 1 mole amount of substance each are allowed to mix at a temperature of 20°C. (b) How much energy has been dissipated? (c) Where does the energy used for producing entropy come from?

SOLUTION: We can use Equ.(6.59) directly. The total amount of substance is 2 mole, and the molar fractions are both 0.5. Therefore:

$$S_2 - S_1 = -n\left\{\bar{x}_A R \ln\left(\bar{x}_A\right) + \bar{x}_B R \ln\left(\bar{x}_B\right)\right\}$$
$$= -2\,\text{mole} \cdot 8.31\,\text{J}/(\text{mole}\cdot\text{K})\left\{0.5\ln\left(0.5\right) + 0.5\ln\left(0.5\right)\right\} = 11.5\,\text{J}/\text{K}$$

The energy dissipated is 11.5 J/K · 293 K = 3.38 kJ.

(c) The chemical potential of each of the substances changes since the pressure of a component changes from P to its partial pressure. In this process of diffusion, energy is released which—under the present circumstances—is dissipated.

EXAMPLE 6.14. Pressure coefficient and partial molar volume.

(a) Determine the pressure coefficient of pure iron. The density of iron is 7874 kg/m^3, and its molar mass is 0.0559 kg/mole. (b) The pressure coefficient of ammonia dissolved in water is $24.1 \cdot 10^{-6}$ G/Pa for standard conditions. Determine its partial molar volume and the equivalent density.

SOLUTION: (a) The pressure coefficient of the chemical potential is the (partial) molar volume of the substance. The latter is related to the density by

$$\beta_\mu = \bar{v} = \frac{V}{n} = M_0 \frac{V}{m} = M_0 \frac{1}{\rho} = 0.0559 \frac{1}{7874} \frac{\text{m}^3}{\text{mole}} = 7.10 \cdot 10^{-6} \frac{\text{m}^3}{\text{mole}}$$

The unit is equivalent to G/Pa.

(b) The partial molar volume can be determined from the pressure coefficient:

$$\bar{v} = \beta_\mu = 24.1 \cdot 10^{-6} \text{G} / \text{Pa}$$

Ammonia (NH_3) has a molar mass of 0.017 kg/mole. The equivalent density is

$$\rho = M_0 \frac{1}{\bar{v}} = 0.017 \frac{1}{24.1 \cdot 10^{-6}} \text{kg} / \text{m}^3 = 705 \text{kg} / \text{m}^3$$

Ammonia dissolved in water without dissociating behaves as if it had a density slightly smaller than that of water. Put differently, if 705 kg of ammonia are dissolved in a vast amount of water, the volume of the mixture will increase by 1 m^3.

EXAMPLE 6.15. Temperature coefficients and entropy of phase change.

(a) Show that the temperature coefficients of the chemical potential of a substance can be used to determine the (molar) entropy of phase change. Use the values for water to calculate the entropy of fusion (melting). (b) In standard tables, coefficients are given for 25°C. Ice melts at 0°C. How do we have to correct for this temperature difference?

SOLUTION: (a) The temperature coefficient of the chemical potential of a substance is equal to its negative molar entropy (Equ.(6.44)). Therefore, we have

$$\bar{s}_{change} = \bar{s}_{phase2} - \bar{s}_{phase1} = -\left(\alpha_{\mu 2} - \alpha_{\mu 1}\right)$$

Values for water (1) and ice (2) can be taken from Table 6.2:

$$\bar{s}_{f,\text{H2O}} = -\left(-69.9 - \left(-44.8\right)\right) \frac{\text{J}}{\text{K} \cdot \text{mole}} = 25.1 \frac{\text{J}}{\text{K} \cdot \text{mole}}$$

(b) The temperature coefficients are (negative) molar entropies. The entropy of a simple substance such as ice or water changes with temperature according to the entropy capacitance:

$$\bar{s}\left(T\right) = \bar{s}\left(T_0\right) + \bar{\kappa}_S\left(T - T_0\right)$$

The molar entropy capacitance of water is about 0.27 J/(K^2·mole), for ice it is about half this value. The molar entropies of water and of ice at 0°C turn out to be about 63.2 J/(K · mole) and 41.5 J/(K · mole), respectively. The corrected value of the molar entropy of fusion (melting) of H_2O is now closer to 22 J/(K · mole), close to the accepted value.

EXAMPLE 6.16. Humidity of saturated air.

At 25°C and a pressure of 1.013 bar, how much water vapor is in air, at most? The air is in contact with a water reservoir at the same standard conditions.

SOLUTION: Assume the air were completely dry. Then, water would evaporate since the chemical potential of liquid water is higher than that of (no) vapor in the air. The transfer should end when the chemical potential have become equal:

$$\mu_{water}\left(T_0,P_0\right)=\mu_{vapor}\left(T_0,P_{vapor}\right)$$

P_{vapor} is the pressure of the water in the air (its partial pressure). The vapor will be treated as an ideal gas having a part of the pressure of the air:

$$\mu_{water}\left(T_0,P_0\right)=\mu_{vapor}\left(T_0,P_0\right)+RT\ln\left(\frac{P_{vapor}}{P_0}\right)$$

Numerical values yield

$$\begin{aligned}P_{vapor}&=P_0\exp\left[\frac{1}{RT}\left(\mu_{water}\left(T_0,P_0\right)-\mu_{vapor}\left(T_0,P_0\right)\right)\right]\\&=1.013\,\text{bar}\cdot\exp\left(\frac{1}{8.314\cdot 298}\left(-237180-\left(-228600\right)\right)\right)=0.0317\,\text{bar}\end{aligned}$$

This is the partial pressure of water vapor in air, i.e. about 3.1% of standard pressure. This means also that 3.1% of the amount of substance of air is water vapor. On a mass basis, we obtain

$$\begin{aligned}m_{vapor}&=M_{0,H2O}n_{vapor}=0.031M_{0,\mathrm{H2O}}n_{air}\\&=0.031\frac{M_{0,\mathrm{H2O}}}{M_{0,air}}m_{air}=0.031\frac{0.018}{0.029}m_{air}=0.019m_{air}\end{aligned}$$

19 g of water per kilogram of air at standard conditions. Note that this number has two meanings. For one, it is the maximum amount of water that can be contained in air—if air is saturated it contains this much water. Second, it is the vapor pressure of water at 25°C and 1.013 bar. Normally, air is not saturated which means that a body of water can continue to evaporate in the open.

EXAMPLE 6.17. Salt lowers the freezing point of water.

A certain amount of table salt (NaCl) is dissolved in freezing water. By how much is the freezing point changed?

SOLUTION: Without salt, ice freezes at 0°C, i.e., the chemical potentials of the pure substances are equal at this point. Salt and the change of temperature lead to a change of chemical potential of water; however, the potential of ice is changed only because of the change of temperature. With the added salt, at the new temperature, the chemical potentials are again equal. If we use 0°C and no salt as the reference point of our considerations, the condition of equilibrium is

$$\mu_{water}\left(T=0°\text{C},P_0,\bar{c}_{salt}=0\right)-RT\frac{2n_{salt}}{n_{water}}+\alpha_{\mu,water}\Delta T=\mu_{ice}\left(T=0°\text{C},P_0\right)+\alpha_{\mu,ice}\Delta T$$

NaCl dissociates into two ions which leads to the factor of 2 multiplying the amount of salt. Since the chemical potentials of water and ice are equal at 0°C, we have

$$\Delta T=\frac{1}{\alpha_{\mu,water}-\alpha_{\mu,ice}}RT\frac{2n_{salt}}{n_{water}}=\frac{2\cdot 8.314\cdot 273}{-69.9-(-44.8)}\frac{n_{salt}}{n_{water}}=-181\,\text{K}\frac{n_{salt}}{n_{water}}$$
$$=-181\,\text{K}\frac{M_{0,water}}{M_{0,salt}}\frac{m_{salt}}{m_{water}}=-55.7\,\text{K}\frac{m_{salt}}{m_{water}}$$

Remember that the temperature coefficients are the (negative) molar entropies of water and ice. Their difference is the molar entropy of fusion (of melting) of H_2O. For a molar fraction of salt of 0.01 (corresponding to a little more than 30 g of salt per liter of water), the melting point is depressed by about 2°C.

EXAMPLE 6.18. Dissolved oxygen in water.

Oxygen gas (O_2) is dissolved in water. This circumstance is important for aquatic life. We want to know how much oxygen will be in the (surface) water of a stream, lake, or the ocean. (a) Calculate the equilibrium concentration of O_2 in pure water if the water is in contact with an atmosphere composed only of oxygen. (b) What will the actual value for our atmosphere be?

SOLUTION: Similar to the example of humidity in the air (Example 6.16), we consider the chemical equilibrium between O_2 in the air and O_2 dissolved in water:

$$\mu_{\text{O2}(aq)}\left(T_0,\bar{c}_{\text{CO2}(aq)}\right)=\mu_{\text{O2}(gas)}\left(T_0,P_{\text{O2}(gas)}\right)$$

The chemical potential of O_2 in water is determined by its concentration. In air, it is determined by its (partial) pressure:

$$\mu_{\text{O2}(aq)}\left(T_0,\bar{c}^0_{\text{O2}(aq)}\right)+RT\ln\left(\frac{\bar{c}_{\text{O2}(aq)}}{\bar{c}^0_{\text{O2}(aq)}}\right)=\mu_{\text{O2}(gas)}\left(T_0,P_0\right)+RT\ln\left(\frac{P_{\text{O2}(gas)}}{P_0}\right)$$

(a) If the atmosphere is pure oxygen gas, the (partial) pressure of O_2 is 1 atm ($1.013\cdot 10^5$ Pa). The previous equation can be transformed to yield the ration of concentration of O_2 in water and the standard concentration (1 mole/L = 1000 mole/m^3):

$$\frac{\bar{c}_{\text{O2}(aq)}}{\bar{c}^0_{\text{O2}(aq)}}=\exp\left[\frac{1}{RT}\left(-\mu_{\text{O2}(aq)}\left(T_0,\bar{c}^0_{\text{O2}(aq)}\right)+\mu_{\text{O2}(gas)}\left(T_0,P_0\right)+RT\ln(1)\right)\right]$$
$$=\exp\left[\frac{1}{8.314\cdot 298}(-16440-0)\right]=\exp(-6.63)=1.31\cdot 10^{-3}$$

(b) We need to know the partial pressure of O_2 in the actual atmosphere. For ideal gases, the fraction of volume taken by a component is also the fraction of the total pressure. So, the partial pressure of O_2 in the air is $0.2\cdot 10^5$ Pa. Therefore:

$$\frac{\bar{c}_{\text{O2}(aq)}}{\bar{c}^0_{\text{O2}(aq)}}=\exp\left[\frac{1}{RT}\left(-\mu_{\text{O2}(aq)}\left(T_0,\bar{c}^0_{\text{O2}(aq)}\right)+\mu_{\text{O2}(gas)}\left(T_0,P_0\right)+RT\ln(0.2)\right)\right]$$

or

$$\frac{\bar{c}_{O2(aq)}}{\bar{c}^0_{O2(aq)}} = \exp\left[\frac{1}{8.314 \cdot 298}\left(-16440 - 0 + 8.314 \cdot 298 \cdot \ln(0.2)\right)\right] = \exp(-8.25) = 2.63 \cdot 10^{-4}$$

This corresponds to 0.26 mole of oxygen gas per cubic meter of water. The result is approximately equal to 20% of the concentration obtained for a pure oxygen atmosphere. Note that these results have been obtained for pure water. Ocean water, in particular, contains many other dissolved substances that substantially alter the chemistry of the fluid.

EXAMPLE 6.19. Solubility of gases: Henry's law.

Consider an atmosphere containing different gases in contact with a liquid such as water. Experience like the one reported in Fig. 6.2 shows that the amount of a gas dissolved in water is proportional to the partial pressure of the gas in the atmosphere. This is sometimes reported by saying that the pressure P_g of the component in the atmosphere is proportional to the mole fraction x of the gas as a solute, which is Henry's law:

$$P_g = K_x x$$

Show that this relation follows from our previous considerations and express the constant K_x using the chemical potentials.

SOLUTION: As in Example 6.18, we begin by assuming that the gas in the atmosphere and the gas dissolved in the liquid are in equilibrium:

$$\mu_g^0 + RT \ln\left(\frac{P_g}{P_0}\right) = \mu_{aq}^0 + RT \ln\left(\frac{\bar{c}_{aq}}{\bar{c}^0_{aq}}\right)$$

Therefore:

$$\mu_g^0 - \mu_{aq}^0 = RT \ln\left(\frac{\bar{c}_{aq}}{\bar{c}^0_{aq}} \frac{P_0}{P_g}\right)$$

Now, the expression of Henry's law is introduced, and the definition of the mole fraction is applied. For dilute solutions this leads to

$$\begin{aligned}\mu_g^0 - \mu_{aq}^0 &= RT \ln\left(\frac{\bar{c}_{aq}}{\bar{c}^0_{aq}} \frac{P_0}{K_x x}\right) = RT \ln\left(\frac{\bar{c}_{aq}}{\bar{c}^0_{aq}} \frac{P_0 n_f}{K_x n_s}\right) \\ &= RT \ln\left(\frac{n_s}{V} \frac{1}{\bar{c}^0_{aq}} \frac{P_0 n_f}{K_x n_s}\right) = RT \ln\left(\frac{P_0}{\bar{c}^0_{aq}} \frac{1}{K_x} \frac{n_f}{V}\right)\end{aligned}$$

where n_f/V is the concentration of the solvent. (For water, it is 55500 mole/m^3.) From this we obtain the result for K_x:

$$\ln(K_x) = -\frac{\mu_g^0 - \mu_{aq}^0}{RT} + \ln\left(\frac{P_0}{\bar{c}^0_{aq}} \frac{n_f}{V}\right)$$

For carbon dioxide dissolved in water, K_x is $1.66 \cdot 10^8$ Pa, while for hydrogen gas, it turns out to be $7.10 \cdot 10^9$ Pa. The latter number means that in an atmosphere of hydrogen at 1 atm, the mole fraction of dissolved gas would be $1.4 \cdot 10^{-5}$.

EXAMPLE 6.20. Ion transport across a membrane: The Nernst potential.

Assume that an ionic substance is found on both sides of a membrane (as in Fig. 6.28) and that it can cross the membrane. The liquid in which it is dissolved is the same in both environments. If the ions attain densities c_{I} and c_{II} in their environments, what must the voltage established due to this distribution be?

SOLUTION: We assume the distribution of ions in the environments to be in electrochemical equilibrium:

$$\mu_{EC,\mathrm{I}} = \mu_{EC,\mathrm{II}}$$

In this case, Equ.(6.38) for the electrochemical potential and Equ.(6.62) for the chemical potential of a solute yield

$$\left[\mu + z\,\mathcal{F}\varphi\right]_{\mathrm{I}} = \left[\mu + z\,\mathcal{F}\varphi\right]_{\mathrm{II}}$$
$$\mu\left(T,\bar{c}_o\right) + RT\ln\left(\frac{\bar{c}_{\mathrm{I}}}{\bar{c}_o}\right) + z\,\mathcal{F}\varphi_{\mathrm{I}} = \mu\left(T,\bar{c}_o\right) + RT\ln\left(\frac{\bar{c}_{\mathrm{II}}}{\bar{c}_o}\right) + z\,\mathcal{F}\varphi_{\mathrm{II}}$$
$$U = \varphi_{\mathrm{I}} - \varphi_{\mathrm{II}} = \frac{RT}{z\,\mathcal{F}}\ln\left(\frac{\bar{c}_{\mathrm{II}}}{\bar{c}_{\mathrm{I}}}\right)$$

This expression is called the Nernst potential. Since we normally have several ionic species involved in electrochemical processes in biology, the actual voltage is calculated differently.[7]

6.7 TRANSPORT OF SUBSTANCES

In this and the next section, I will formulate some simple dynamical—or as they are called in chemistry, kinetic—models to demonstrate how our previous work applies. The models presented in Section 6.2 can now be put on a more secure footing. I will start with transports and then treat reactions in Section 6.8.

Substances can flow—or be transported—in two different ways. First, they can migrate by themselves *through* materials. This is called diffusion or conduction. Second, they can be transported *with* other materials, such as water, in which they are contained. This is called convection, a process which will be considered in more detail in Chapter 8. The diffusion of a substance or the transport of a "carrier substance" in convection are driven by chemical potential differences.

6.7.1 Laws of Balance and Dynamical Models

Since we are going to consider only transports and no reactions at this point, the law of balance of a single species in a single compartment is

$$\frac{dn}{dt} = I_{n,cond} + I_{n,conv} \tag{6.67}$$

Dynamical models are obtained by introducing the flows of a species into its law of balance. An example was formulated in Equ.(6.1).

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[7] J. Malmivuo and R. Plonsey (1995): Chapter 3.

6.7.2 Diffusion

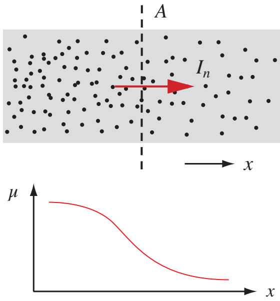

Figure 6.34: Substances diffuse from places where the chemical potential is high (due to high concentration) to places where the potential is lower.

Imagine particles with a concentration $\bar{c}$ in a uniform environment (such as a gel or a liquid solvent). The chemical driving force is pulling or pushing the particles which, since they are in a resistive medium, will quickly attain a certain drift speed. The current of amount of substance due to diffusion of these particles is equal to the product of cross section A, concentration $\bar{c}$, and drift speed v_d (Fig. 6.34):

$$I_n = A\bar{c}\,v_d \tag{6.68}$$

The drift speed is modeled as the result of a chemical driving force $\Delta\mu = \mu(x_2) - \mu(x_1)$. At the same time, it is proportional to the mechanical forces on the particles[8] (which are in balance). A simple application of the balance of energy tells us that $n\Delta\mu = nF_d\Delta x$, so the force on a particle and therefore the drift speed should be proportional to the driving force per unit distance: $v_d = k_D\Delta\mu/\Delta x$ (with a diffusion factor k_D). Therefore, we obtain

$$I_n = -k_D A\bar{c}\,\frac{\Delta\mu}{\Delta x}$$

$\Delta\mu/\Delta x$ is called the *gradient of the chemical potential*. The minus sign indicates that the flow is positive in the direction of the diffusing substance's decreasing chemical potential. In a general case, the gradient varies from point to point (Fig. 6.34). Graphically, it corresponds to the slope of the μ-x curve. In a single spatial dimension, this can be written as the derivative of the chemical potential with respect to position:

$$I_n = -k_D A\bar{c}\,\frac{d\mu}{dx} \tag{6.69}$$

Note that the current is proportional to the concentration and the chemical potential difference or, in the spatially continuous case, the gradient of the potential. This is a form we had anticipated in Equ.(6.1) for the model of the diffusion of toluene.

The chemical potential of the diffusing substance can be assumed to obey the logarithmic relation derived in Equ.(6.62). Inserting this into Equ.(6.69) yields

$$I_n = -k_D A\bar{c}\,\frac{d}{dx}\left(\mu\left(T,\bar{c}_0\right) + RT\,\ln\left(\frac{\bar{c}}{\bar{c}_0}\right)\right) = -k_D ART\,\frac{d\bar{c}}{dx}$$

If we divide the current by the cross section through which it flows, we obtain the *current density* of amount of substance. The resulting relation is the usual form of Fick's law for diffusion:

$$j_n = -D\,\frac{d\bar{c}}{dx} \tag{6.70}$$

$D = k_D RT$ is called the diffusion constant or *diffusivity*. The term $d\bar{c}/dx$ is the *concen-*

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[8] This assumes a medium in which the mechanical effect is due to viscosity in a way that leads to linear effects (see Chapter 3).

tration gradient. It can be replaced by $\Delta\bar{c}/\Delta x$ for intervals where the molar concentration changes linearly with position. Note that Equ.(6.70) is analogous to Ohm's law (Chapter 1) or Fourier's law (Chapter 7).

Equ.(6.70) is a form of a constitutive law for spatially continuous systems which we will treat in Parts III and IV of this book. Here is a simple way to apply diffusive relations in spatially uniform dynamical systems. We already encountered this phenomenon in Chapter 1 (Section 1.5.3) when we discussed chains of *RC* systems such as chains of communicating tanks. The tanks represent storage elements whereas the pipes allow for flows between the tanks. The flows are made dependent upon the difference of potentials of two neighboring storage elements. This is exactly what we are dealing with in the case of diffusion. Material elements of the substrate through which the dissolved species migrates serve as storage devices. The quantity of substance contained in an element is responsible for the chemical potential whose difference is responsible for the flows between elements. This defines the structure of simple uniform dynamical models consisting of parts (elements) of the larger system (Fig. 6.35).

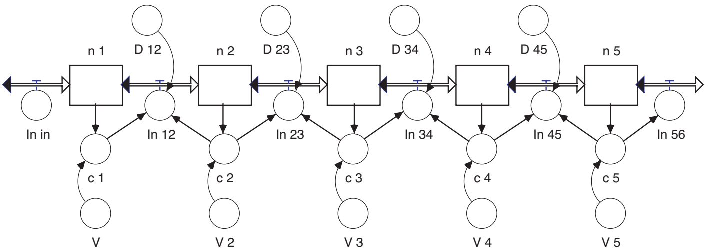

Figure 6.35: Model diagram of diffusion in a single spatial direction. The system has been divided into several elements each of which is treated as uniform.

The role of concentration. Why should the transport of substance be proportional to the concentration of the diffusing substance (Equ.(6.69))? Isn't it enough that the chemical potential depends upon concentration? Actually, the chemical driving force, i.e., a difference of potentials, depends upon the (logarithm of) the ratio of the concentrations at two points 1 and 2 along the path of the diffusing species:

$$\Delta\mu = \left(\mu^0 + RT\,\ln\left(\frac{\bar{c}_2}{\bar{c}_0}\right)\right) - \left(\mu^0 + RT\,\ln\left(\frac{\bar{c}_1}{\bar{c}_0}\right)\right) = RT\,\ln\left(\frac{\bar{c}_2}{\bar{c}_1}\right)$$

No matter if $\mu_1 = 2$ and $\mu_2 = 1$, or $\mu_1 = 0.002$ and $\mu_2 = 0.001$, the driving force is the same, but the diffusive current of substance must be 1000 time stronger in the first case, so we need to make it dependent upon the concentration of the dissolved species. Obviously, the microscopic argument I used in this section to work out the expressions for diffusion (Equ.(6.68) and Equ.(6.69)) are not needed to suggest a useful form for the transport of dissolved substances.

Diffusion of charge and entropy have already made their debut on our stage (Chapters 1 and 4). Diffusion of charge will be picked up again in Chapter 13. The latter case—conduction of entropy—will be considered in more detail in Chapters 7 and 13.

6.7.3 Transport between different environments

Substances flow from one environment into another as long as there is a difference of the chemical potentials of the substance in these environments. In analogy to what we have done already, let me assume the following form for the current of substance from environment I to II (Fig. 6.36):

$$I_{n,\mathrm{I}\to\mathrm{II}} = k' A \bar{c}_{\mathrm{I}} \Delta\mu_{\mathrm{I}\to\mathrm{II}} \tag{6.71}$$

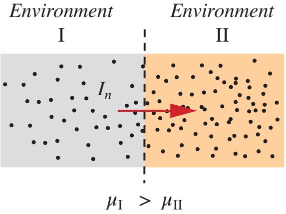

Figure 6.36: Diffusive transport of a substance from one environment into another (such as from water to air, or from soil to water) is caused by a chemical potential difference. The substance can diffuse from an environment where the concentration is low to one where it is high.

If the substance is dissolved, its chemical potential depends logarithmically upon its concentration and upon a reference value which will be different for different environments (Fig. 6.36). We have seen the importance of the distribution of the diffusing substance, which is established after the flows have stopped. This suggests using the equilibrium condition as the reference point for calculating potentials:

$$\Delta\mu_{\mathrm{I}\to\mathrm{II}} = \mu_{\mathrm{II}}^{eq} - \mu_{\mathrm{I}}^{eq} + RT \ln\left(\frac{\bar{c}_{\mathrm{II}}}{\bar{c}_{\mathrm{II}}^{eq}}\right) - RT \ln\left(\frac{\bar{c}_{\mathrm{I}}}{\bar{c}_{\mathrm{I}}^{eq}}\right)$$

Since the equilibrium values of the potential of the substance in environments I and II are equal, the chemical driving force turns out to be equal to

$$\Delta\mu_{\mathrm{I}\to\mathrm{II}} = RT \ln\left(\frac{\bar{c}_{\mathrm{II}}}{\bar{c}_{\mathrm{II}}^{eq}} \frac{\bar{c}_{\mathrm{I}}^{eq}}{\bar{c}_{\mathrm{I}}}\right) \tag{6.72}$$

The current of substance can be obtained by inserting this expression into Equ.(6.71):

$$I_{n,\mathrm{I}\to\mathrm{II}} = k' A \bar{c}_{\mathrm{I}} RT \ln\left(\frac{\bar{c}_{\mathrm{II}}}{\bar{c}_{\mathrm{II}}^{eq}} \frac{\bar{c}_{\mathrm{I}}^{eq}}{\bar{c}_{\mathrm{I}}}\right) \tag{6.73}$$

Conditions near equilibrium. The condition of equilibrium has been chosen as the reference point for calculating the chemical potential. I and II refer to the substance in environments I and II. The difference of chemical potentials in equilibrium must be zero, which is indeed the case. (Note the difference between this result and the assumption made in Equ.(6.2). There we did not know about the form of the chemical potential of a dilute substance—I made an intuitive guess as to how the driving force might depend upon concentrations relative to their equilibrium values.) Interestingly, Equ.(6.73) turns into Equ.(6.2) for conditions near equilibrium. This is one reason to consider conditions which do not deviate much from equilibrium where the ratio of a concentration to its equilibrium value is close to 1.[9]For small deviations from equilibrium, the logarithm ln(x) becomes $x - 1$. Therefore

$$I_{n,\mathrm{I}\to\mathrm{II}} = k' ART\, \bar{c}_{\mathrm{I}}\left(\frac{\bar{c}_{\mathrm{II}}}{\bar{c}_{\mathrm{II}}^{eq}} \frac{\bar{c}_{\mathrm{I}}^{eq}}{\bar{c}_{\mathrm{I}}} - 1\right) = k' ART\left(\frac{\bar{c}_{\mathrm{I}}^{eq}}{\bar{c}_{\mathrm{II}}^{eq}} \bar{c}_{\mathrm{II}} - \bar{c}_{\mathrm{I}}\right)$$

The ratio of the concentration at equilibrium in environment II to the one in environment I is called the *equilibrium constant* $\mathcal{K}$:

$$\mathcal{K} = \frac{\bar{c}_{\mathrm{II}}^{eq}}{\bar{c}_{\mathrm{I}}^{eq}} \tag{6.74}$$

If we use this definition, the transport law for a species flowing from an environment into a chemically different one can be written as follows:

$$j_{n,(\mathrm{I}\rightarrow\mathrm{II})} = k\left(\bar{c}_{\mathrm{II}} - \mathcal{K}\bar{c}_{\mathrm{I}}\right) \qquad \textbf{(6.75)}$$

$k = k'RT\,\mathcal{K}^{-1}$ is a transport coefficient. It is often called *permeability*. One example is the case of a membrane separating environments I and II. The name is also used for permeability of rocks or for water permeability of membranes in osmosis (see Section 6.7.4) and has an analogous meanings (details naturally vary).

Nonlinear equilibrium relations. The definition of the equilibrium constant in the form of Equ.(6.74) assumes a linear relation between concentrations in equilibrium such as the one found for toluene in water and air (Fig. 6.2, right). When the equilibrium relation is not constant, such as for toluene in water and soil (Fig. 6.37), the expression in Equ.(6.75) can be generalized. For this example, the term in parentheses in Equ.(6.75) could be changed to something like $c_w - \mathcal{K}c_s{}^a$.

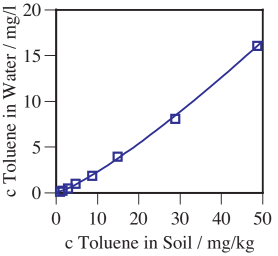

Figure 6.37: Relation of equilibrium concenrations of toluene in water and soil. It is clearly nonlinear. Note the different forms applied to measures of concentration (mg/L for water, mg/kg for soil).

Linearity or nonlinearity of chemical processes? Even if the relations Equ.(6.75) and Equ.(6.71) (with Equ.(6.72)) are identical near equilibrium, they are different in general. So, the question arises if one of them is better in general. It turns out that the expression which is linear in the concentrations, i.e., Equ.(6.75), often fits the data better. In other words, our assumption that the rates at which chemical processes proceed are linear in the chemical driving force, need not apply. We know from our work on electric and thermal phenomena that linear dependence upon driving forces often leads to good results, but this is by no means always the case. Just remember turbulent flow or charge transport in diodes. I will resume the discussion of the dependence of rates of chemical processes upon the difference of chemical potentials in more detail when we turn to models of reactions (Section 6.8).

6.7.4 Osmosis: Soaking Dried Lentils

When dried lentils are soaked, they take in water and their volume grows. It turns out that at least a part of the phenomenon can be understood in terms of chemical process-

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9. Another reason are kinetic (microscopic) models similar to the one used above in the discussion of diffusion. Microscopic models suggest relations such as Equ.(6.75). The reasoning roughly goes as follows. Imagine particles of a substance in two environments, I and II. The particles in each compartment have a tendency to move into the other environment:

$$\begin{aligned} I_{n,\mathrm{I}\rightarrow\mathrm{II}} &= -k_{\mathrm{I}\rightarrow\mathrm{II}} A\,\bar{c}_{\mathrm{I}} \\ I_{n,\mathrm{II}\rightarrow\mathrm{I}} &= -k_{\mathrm{II}\rightarrow\mathrm{I}} A\,\bar{c}_{\mathrm{II}} \end{aligned}$$

The net flow with respect to compartment I will be

$$\begin{aligned} I_n = I_{n,\mathrm{I}\rightarrow\mathrm{II}} - I_{n,\mathrm{II}\rightarrow\mathrm{I}} &= -k_{\mathrm{I}\rightarrow\mathrm{II}} A\bar{c}_{\mathrm{I}} + k_{\mathrm{II}\rightarrow\mathrm{I}} A\bar{c}_{\mathrm{II}} \\ &= -k_{\mathrm{I}\rightarrow\mathrm{II}} A\left(\bar{c}_{\mathrm{I}} - \frac{k_{\mathrm{II}\rightarrow\mathrm{I}}}{k_{\mathrm{I}\rightarrow\mathrm{II}}}\bar{c}_{\mathrm{II}}\right) \end{aligned}$$

which is similar to our Equ.(6.75). So here we image two simultaneous opposing flows, each with its own flow constant, rather than a single current which is determined by the chemical driving force.

es. However, a first model will have to be augmented by ideas that make use of our understanding of the dynamics of fluids discussed in Chapter 1.

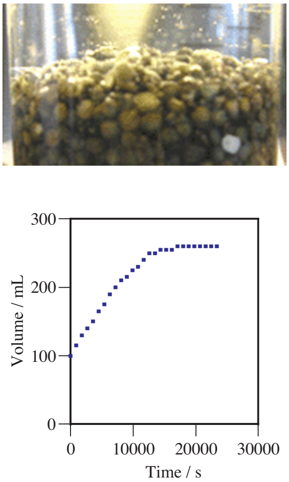

Figure 6.38: Volume of lentils soaking in distilled water, as a function of time. Data were taken every 15 minutes by eye using the markings on the container.

Experiment, observations, and a basic idea. Dried brown lentils are put in a container with plenty of distilled water (see Fig. 6.38, top). In the course of time, their volume grows to about 2.6 times the initial value (see the graph in Fig. 6.38).

The fundamental process must be intake of water. We assume the increase in volume of the legumes to be due only to the added amount of water. Therefore, we can attempt to understand their swelling in terms of a single law of balance of volume applied to their water content:

$$\dot{V}_{lentils} = I_{V,water} \tag{6.76}$$

(see Fig. 6.39). The important task is to model the flow of water into the lentils. The phenomena discussed before in Section 6.1 suggest that the flow may be due to osmosis: The pressure of the remaining water in the dried lentils (and therefore its chemical potential) is smaller than the pressure of the water outside (i.e., its chemical potential). The chemical potential difference is the driving force for the flow of water. As the water content in the lentils increases, the concentration of the solutes in the cells decreases. We have seen that solutes reduce the chemical potential (pressure) of the solvent (Section 6.6.4). When the concentration is reduced, the reduction of pressure must be smaller. Therefore, in the course of time, the pressure difference between outside and inside will decrease, letting the current of water decrease.

Water pressure: Osmosis. As before, we should assume the flow of amount of water to depend upon the chemical driving force:

$$I_{n,water} = k' A\left(\mu_{outside} - \mu_{inside}\right) \tag{6.77}$$

k'A is a chemical conductance. Alternatively, the expression can be put in hydraulic form to fit the law of balance in Equ.(6.76):

$$I_{V,water} = kA\left(P_{outside} - P_{inside}\right) \tag{6.78}$$

The water pressure inside dried lentils is smaller than on the outside since substances are dissolved in the remaining water. According to Section 6.6.4, the reduction of pressure is proportional to the density of dissolved substances. Therefore:

$$P_{inside} = 1 - P_{solute} = 1 - a\frac{n_{solute}}{V_{water}} \tag{6.79}$$

We can leave the pressure values arbitrary by setting $P_{outside} = 1$. n_{inside} is the amount of solutes inside the lentils. Remember that we set the pressure of pure water equal to 1. The product $a \cdot n_{inside}$ is unknown and should be determined by comparing simulation results to data (Fig. 6.38).

We will assume that the shape of the lentils will be like a pillbox whose height does not change much. This makes the surface area of the lentils proportional to their volume. We do not have to worry about the value of the factor of proportionality—changing it will change the flow constant *k* in Equ.(6.78) which has to be found by simulation by the same factor.

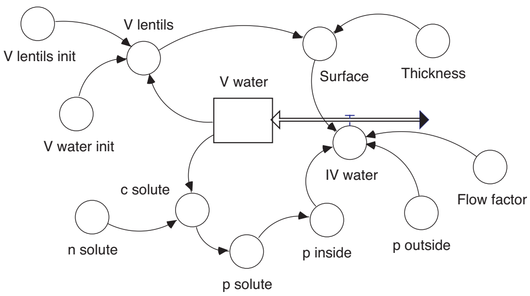

Figure 6.39: Diagram of a first system dynamics model of the soaking of lentils. Note the balance of amount of water, and two effects upon the flow: (1) Pressure difference because of solutes in the lentils, and (2) change of surface due to change of volume.

If we choose an amount of initial water in the dried lentils of 25 (25% of the 100 mL of the initial volume of lentils), simulation of the model results in a function shown in Fig. 6.40 (dashed line). It turns out that the simulation fits the initial rise of volume. However, the model predicts that the lentils continue to grow, contrary to what is observed in the experiment. What is the reason for this discrepancy?

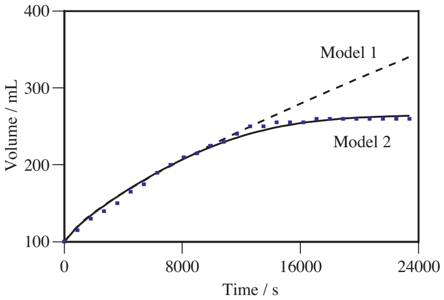

Figure 6.40: Simulation results for the first and second models, and data (dots). A second effect upon the pressure of the water inside the lentils has been taken into account (pressure due to the elasticity of the cell walls).

Water pressure: Elastic walls. The chemical factor—solution of substances in the water inside the lentils—is not the only one affecting the pressure of the liquid. In the lentils, the water is contained in cells which act as storage elements having elastic walls. We know this condition as a capacitive effect (Chapter 1): increasing the amount of water raises the pressure. Combining chemical and capacitive effects means that

$$P_{inside} = 1 - P_{solute} + P_{elastic} \tag{6.80}$$

Let us assume that the capacitive component of pressure is zero when the lentils are dried and rises steeply when the cell walls are stretched strongly. A nonlinear capacitive relation of the form

$$P_{elastic} = b\left(V_{water} - V_{water,initial}\right)^4 \tag{6.81}$$

can accommodate these ideas and results in a simulation that follows our experimental data fairly well (see the solid curve in Fig. 6.40).

QUESTIONS

36. Why is the diffusive current of substance proportional to the concentration of the species?

37. Imagine a substance that “prefers” to be in environment I rather than in environment II. Is the equilibrium constant larger than 1, or smaller than 1?
38. What happens to the flux of amount of substance between two different environments when the condition $c_{II} = \mathcal{K} c_I$ applies?
39. Why are Equ.(6.77) and Equ.(6.78) equivalent?
40. Consider the model of soaking of lentils that makes the flow dependent upon osmotic pressure only. Why does the volume not level off in this model?

EXAMPLE 6.21. Permeability of red blood cells.

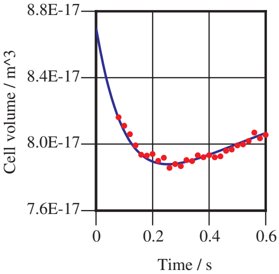

Figure Ex.21

Consider the phenomenon described in Section 6.1 (Fig. 6.5): Red blood cells are placed in an isotonic solution (bath) having a molar concentration of solute of 300 mole/m^3. Then, a substance is dissolved in the bath that raises the concentration to 600 mole/m^3. This substance can diffuse through the cell membranes into the cells.

A single cell has an initial volume of $8.7 \cdot 10^{-17}$ m^3 (see Fig. Ex.21). The volume decreases quickly at first (within the first 0.25 s), then it recovers more slowly to its initial value (Fig. 6.5).

(a) Write the laws of balance of the substances that need to be considered to understand this phenomenon. (b) Express the transports by constitutive laws. (c) Use the graph to determine the current of water at $t = 0$ s. Use this to find the permeability of the cell walls for water. (d) If the substance dissolved in the bath could not diffuse into the cells, what would happen to their volume? (e) Take the actual case. What can we say about the flow of water when the volume has reached its minimal value at $t = 0.25$ s? What does this mean for the concentration of solutes in the cell? How much of the dissolved substance has moved from the bath into a cell? Use this to estimate the permeability of the cell walls for the diffusing substance.

SOLUTION: (a) In this model, two substances have to be considered, water (w) and the substance added to the bath (s). Each one can flow into or out of the cells:

$$\frac{dV_w}{dt} = I_{V,w} \quad , \quad \frac{dn_s}{dt} = I_{n,s}$$

Each of these equations is supplemented by an initial condition. The model is completed by formulating constitutive laws for the flows.

(b) The transport of water results from osmosis, the transport of the dissolved substance is due to diffusion. Therefore

$$\begin{aligned} I_{V,w} &= k_w A\left(P_{w,outside} - P_{w,inside}\right) \\ &= k_w A\left[\left(P_0 - RT\bar{c}_{outside}\right) - \left(P_0 - RT\bar{c}_{inside}\right)\right] \\ &= -k_w ART\left(\bar{c}_{outside} - \bar{c}_{inside}\right) \\ I_{n,s} &= k_s A\left(\bar{c}_{s,outside} - \bar{c}_{s,inside}\right) \end{aligned}$$

The pressure of the water (whose difference is responsible for the transport of water) is lowered by the presence of dissolved substances (it does not matter, what these substances are). The difference of concentrations of all solutes is, however, equal to the difference of concentrations of the added substance:

$$\bar{c}_{outside} - \bar{c}_{inside} = \bar{c}_{s,outside} - \bar{c}_{s,inside}$$

Diffusion of the substance added to the bath (s) responds only to its own concentration.

(c) The diagram can be used to graphically determine the rate of change of volume which is equal to the current of volume of water (we assume the change of volume of the cells to be determined by the change of volume of water). The graphical result is – $9.4 \cdot 10^{-17}$ m³/s.

The constitutive law for the flow of water can be used to determine the permeability k_w. The surface area of a single cell is $1.4 \cdot 10^{-10}$ m², and the initial difference of concentrations of dissolved substances is equal to the concentration of the added solute, i.e., 300 mole/m³. Therefore

$$k_w = -\frac{I_{V,w}}{RTA\left(\bar{c}_{outside} - \bar{c}_{inside}\right)} = -\frac{-9.4 \cdot 10^{-17}}{8.314 \cdot 298 \cdot 1.4 \cdot 10^{-10} \cdot 300}\frac{\mathrm{m}}{\mathrm{s \cdot Pa}} = 9.0 \cdot 10^{-13}\frac{\mathrm{m}}{\mathrm{s \cdot Pa}}$$

(d) The volume of cells decreases as long as water flows out, and water flows out as long as the concentration of (total) solutes outside is higher than the concentration of (total) solutes on the inside. In the bath, the concentration is 600 mole/m³. This value will be reached in the cells if their volume shrinks to half the initial value (the concentration inside was 300 mole/m³ initially since they were in an isotonic solution at the beginning). The decrease of the volume follows the standard exponential decay curve from V_{init} to $V_{init}/2$.

(e) At $t = 0.25$ s, $I_{V,w} = 0$, therefore, the concentration of (total) solutes inside has reached the outside value of 600 mole/m³. This means

$$\bar{c}_{total,\,inside}\left(t = 0.25s\right) = 600\frac{\mathrm{mole}}{\mathrm{m}^3}$$

$$\bar{c}_{total,\,inside}\left(t = 0.25s\right) = \frac{\bar{c}_{inside,\,init}V_{init} + n_{s,\,inside}\left(t = 0.25s\right)}{V\left(t = 0.25s\right)}$$

$$\begin{aligned} n_{s,\,inside}\left(t = 0.25s\right) &= \bar{c}_{total,\,inside}V\left(t = 0.25s\right) - \bar{c}_{inside,\,init}V_{init} \\ &= 600 \cdot 7.9 \cdot 10^{-17}\,\mathrm{mole} - 300 \cdot 8.7 \cdot 10^{-17}\,\mathrm{mole} = 2.1 \cdot 10^{-14}\,\mathrm{mole} \end{aligned}$$

This amount of the substance *s* that was added to the bath has crossed the cell wall in 0.25 s. Therefore, the average current of amount of substance of *s* is $8.4 \cdot 10^{-14}$ mole/s. Now, at $t = 0.25$ s, the concentration of s inside a cell is already 267 mole/m³, meaning the current must have decreased to a fraction of the initial value. Considering the exponential decay of the current, the initial current should be more than twice the average value. We will take $20 \cdot 10^{-14}$ mole/s. At the beginning, the concentration difference is 300 mole/m³. As a result, the permeability k_s is estimated to be

$$k_s = \frac{I_{n,s}}{A\left(\bar{c}_{s,outside} - \bar{c}_{s,inside}\right)} \approx \frac{20 \cdot 10^{-14}}{1.4 \cdot 10^{-10} \cdot 300}\frac{\mathrm{m}}{\mathrm{s}} = 4.8 \cdot 10^{-6}\frac{\mathrm{m}}{\mathrm{s}}$$

6.8 KINETICS OF CHEMICAL REACTIONS

To describe the dynamics of chemical reactions, we need to be able to express the *production rates* of the species in the equations of balance. The rates are called *reaction rates*. The most important factor affecting these rates are the chemical potentials which depend upon concentrations (naturally, there are many other factors such as pressure and temperature affecting the potentials; however, we will only investigate the role of concentrations of gases or dissolved substances). Apart from the chemical potentials (here: the concentrations), there are parameters facilitating a reaction such as the mobility of the particles. These factors will be considered constant, simply depending upon conditions of the environment of the reacting substances.

6.8.1 Laws of Balance

In general, substances will flow and react. If we neglect flow, we are left with production and destruction resulting form reactions. Reactants will be destroyed (negative production rates) and products will be produced. Sometimes we consider chains of reactions in which case a particular species (numbered *i*) can be produced and destroyed. So, the law of balance of substance *i* will be

$$\frac{dn_i}{dt} = \Pi_{ni,production} + \Pi_{ni,destruction} \tag{6.82}$$

(see also Equ.(6.17)). There will be such an equation for each species appearing in the reactions considered. Since elements are conserved in standard chemical reactions, there is a simple relation between production rates for different species involving the stoichiometric coefficients (Equ.(6.19)).

6.8.2 Reaction Rate for the Conversion A → B

The expressions for production or reaction rates are motivated just as relations for currents of a species from one environment into another are (Section 6.7.3). For a simple reaction A ↔ B (such as the decay of α-glucose, Fig. 6.3) we need to know the decay rate Π_{nA} of the reactant A. Let us consider the density of this reaction rate since it is clear that—if all else is equal—there will be twice as many reactions in twice the volume. This *production rate density* π_{nA} is assumed to depend upon the chemical driving force of the reaction, the concentration of A, and a reaction constant *k'*:

$$\pi_{n,\mathrm{A}} = k'\bar{c}_{\mathrm{A}}\Delta\mu_{\mathrm{A}\to\mathrm{B}} \tag{6.83}$$

If we assume the substances to be gases or dilute solutions, the difference of the chemical potentials can be expressed as

$$\Delta\mu_{\mathrm{A}\to\mathrm{B}} = \mu_{\mathrm{B}}^{eq} - \mu_{\mathrm{A}}^{eq} + RT\,\ln\left(\frac{\bar{c}_{\mathrm{B}}}{\bar{c}_{\mathrm{B}}^{eq}}\right) - RT\,\ln\left(\frac{\bar{c}_{\mathrm{A}}}{\bar{c}_{\mathrm{A}}^{eq}}\right)$$

Just as in the case of transports, I have chosen the equilibrium values of each species as the reference points for calculating the chemical potentials. Since μ_{A} and μ_{B} are the same in equilibrium, this equals

$$\Delta\mu_{\mathrm{A}\to\mathrm{B}} = RT\,\ln\left(\frac{\bar{c}_{\mathrm{B}}}{\bar{c}_{\mathrm{B}}^{eq}}\frac{\bar{c}_{\mathrm{A}}^{eq}}{\bar{c}_{\mathrm{A}}}\right) \tag{6.84}$$

This should be inserted into Equ.(6.83) and multiplied by the volume of the spatially uniform reacting system to yield the reaction rate:

$$\Pi_{n,\mathrm{A}} = Vk'RT\bar{c}_{\mathrm{A}}\,\ln\left(\frac{\bar{c}_{\mathrm{B}}}{\bar{c}_{\mathrm{B}}^{eq}}\frac{\bar{c}_{\mathrm{A}}^{eq}}{\bar{c}_{\mathrm{A}}}\right) \tag{6.85}$$

Note that this expression is negative if the reaction runs from A to B, as we would like it to be. Now, let me apply this to the reaction of α-glucose to β-glucose described in Section 6.1 (Fig. 6.3). The diagram of a system dynamics model may look like the one in Fig. 6.41.

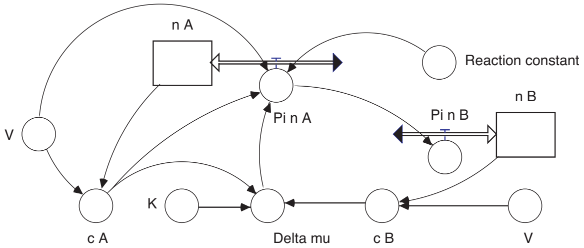

Figure 6.41: Diagram of a system dynamics model of the mutarotation of glucose.

There are two expressions for laws of balance for n_A and n_B. The production rate of A is made dependent upon the concentration of A, the chemical driving force, the volume of the solution, and a reaction constant (the production rate of B is the negative of that for A). The concentrations of A and B are calculated from the amounts of substance n_A and n_B, and the volume. To obtain the differences of chemical potentials, Equ.(6.84) was applied with the ratio $\mathcal{K}$ of equilibrium concentrations

$$\mathcal{K} = \frac{\bar{c}_B^{eq}}{\bar{c}_A^{eq}} \tag{6.86}$$

which—as before in Equ.(6.74)—is called the *equilibrium constant*, this time of the reaction A ↔ B which we have been considering here.

Mutarotation of glucose. Fig. 6.42 (left) shows data of an experiment of mutarotation of glucose and a simulation of the model in Fig. 6.41. Remember the discussion of this phenomenon in Section 6.1 (Fig. 6.3). There is a single substance (α-glucose) that transforms into another (β-glucose). The concrete values used for the simulation are $V = 15 \cdot 10^{-6}$, $k' = 10.8 \cdot 10^{-8}$, all in standard SI units, and $\mathcal{K} = 1.77$. The result is not bad. The equilibrium constant can be fitted perfectly by reading the final amounts or concentrations of the two species (α-glucose and β-glucose). However, the shape of the simulated curves does not agree as well as could be with that of the measurements. This indicates that the form of the assumed constitutive law, Equ.(6.83), is not perfect; the reaction is not linear in the chemical driving force.

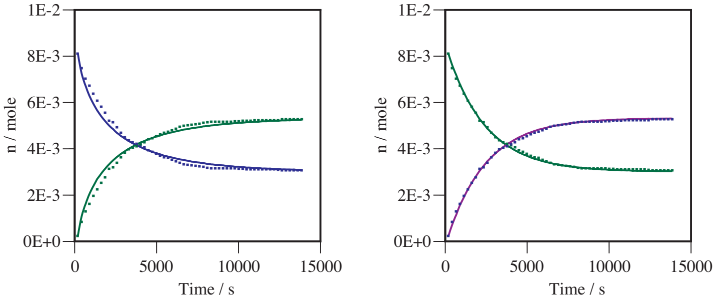

Figure 6.42: Data of the decay of α-glucose and the formation of β-glucose (dots) and simulation results (solid lines). Left: For a model where the reaction rate is made linearly dependent upon the chemical driving force. Right: The reaction rate has been calculated according to Equ.(6.87) which is nonlinear in $\Delta\mu$.

If we use a somewhat different idea,[10] namely

$$\pi_{n,\mathrm{A}} = -k'\bar{c}_{\mathrm{A}} RT\left(1-\exp\left(\frac{1}{RT}\Delta\mu\right)\right) \tag{6.87}$$

we get almost perfect agreement between experiment and model (Fig. 6.42, right). The reason for this expression becomes clear when we introduce Equ.(6.84) and obtain a form of the reaction rate which is analogous to the flow law in Equ.(6.75):

$$\Pi_{n,\mathrm{A}} = Vk\left(\bar{c}_{\mathrm{B}} - \mathcal{K}\bar{c}_{\mathrm{A}}\right) \tag{6.88}$$

We could have obtained this by determining Equ.(6.84) for conditions near equilibrium (as we did for flows in Section 6.7.3). The advantage of Equ.(6.87) over Equ.(6.85) is that the former agrees with Equ.(6.88) also far from equilibrium. Expressions of this form are often successful when applied to kinetic models of simple reactions. We can now summarize the dynamical model for the reaction A ↔ B as follows:

$$\frac{dn_{\mathrm{A}}}{dt} = Vk\left(\bar{c}_{\mathrm{B}} - \mathcal{K}\bar{c}_{\mathrm{A}}\right) \quad , \quad \frac{dn_{\mathrm{B}}}{dt} = -Vk\left(\bar{c}_{\mathrm{B}} - \mathcal{K}\bar{c}_{\mathrm{A}}\right) \tag{6.89}$$

Naturally, we need proper initial values for n_{A} and n_{B} to complement this initial value problem. Because of its linearity, this reaction equation is said to be of *first order*.

6.8.3 Reactions Involving Several Species

A reaction equation such as A + B ↔ C + D tells us that two substances react (and are destroyed) to form two new species. We need to construct an expression for the reaction rate of A (remember that the reaction rates for B, C, and D are then determined as well, Equ.(6.19)). We will take into account the new situation while at the same time adhering to the ideas that led to our previous results. First, the rate will depend upon the chemical driving force which in turn depends upon the concentrations of all four species relative the their equilibrium values. Equ.(6.84) shows that

$$\Delta\mu = RT\,\ln\left(\frac{\bar{c}_{\mathrm{C}}}{\bar{c}_{\mathrm{C}}^{eq}}\frac{\bar{c}_{\mathrm{D}}}{\bar{c}_{\mathrm{D}}^{eq}}\frac{\bar{c}_{\mathrm{A}}^{eq}}{\bar{c}_{\mathrm{A}}}\frac{\bar{c}_{\mathrm{B}}^{eq}}{\bar{c}_{\mathrm{B}}}\right) = RT\,\ln\left(\frac{1}{\mathcal{K}}\frac{\bar{c}_{\mathrm{C}}\bar{c}_{\mathrm{D}}}{\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}}\right) \tag{6.90}$$

where

$$\mathcal{K} = \frac{\bar{c}_{\mathrm{C}}^{eq}\bar{c}_{\mathrm{D}}^{eq}}{\bar{c}_{\mathrm{A}}^{eq}\bar{c}_{\mathrm{B}}^{eq}} \tag{6.91}$$

is the equilibrium constant for the new reaction.

The second important factor is made up of the concentrations of the substances that are disappearing in the reaction. Let them be A and B, i.e., A + B ↔ C + D proceeds from left to right. A reaction between A and B involves the particles of these substances "find" each other, so we should expect the reaction rate to depend upon the product

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10. See Cukrowski, A. S. and Kolbus, A., (2005) for a detailed discussion of ideas concerning rates of chemical reactions.

of their concentrations. Again, the volume comes into play since the reaction is assumed to be homogeneous. Finally, there must be a rate constant that determines the intrinsic speed of the process. If we use the nonlinear form analogous to Equ.(6.87) from the start, we have

$$\pi_{n,\mathrm{A}} = -k'\,\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}RT\left(1-\exp\left(\frac{1}{RT}\Delta\mu\right)\right) \tag{6.92}$$

which, according to Equ.(6.90), is equivalent to

$$\Pi_{n,\mathrm{A}} = V\,k\left(\bar{c}_{\mathrm{C}}\bar{c}_{\mathrm{D}} - \mathcal{K}\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}\right) \tag{6.93}$$

Here, the reaction rate is said to be of *second order*. It is important to note that the examples of reaction rates derived in Equ.(6.88) and Equ.(6.93) are two of the simplest possible forms. As long as reactions lead to equilibria of the form

$$\frac{\bar{c}_{\mathrm{C}}\bar{c}_{\mathrm{D}}}{\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}}\,\frac{\bar{c}_{\mathrm{C}}^{eq}\bar{c}_{\mathrm{D}}^{eq}}{\bar{c}_{\mathrm{A}}^{eq}\bar{c}_{\mathrm{B}}^{eq}} = 1$$

(which itself is just a simple example of its kind; see Section 6.8.6 for a more general result), we can expect reaction equations like the ones derived here. In general, however, reactions are much more complex. They often proceed in several steps from the reactants to the products, where the intermediate reactions might not be known. Therefore, reaction rates often involve powers of the concentrations of the species taking part in the reaction. The exponents, along with the reaction constants k, have to be determined by comparing models and experimental data.

6.8.4 Reactions with Entropy Production and Exchange

Chemical reactions often involve the production, storage, and exchange of entropy. Here is an example that can be investigated experimentally using simple means: The strongly fizzing endothermic reaction of sodium bicarbonate ($NaHCO_3$) in a solution of citric acid ($H_3C_6H_5O_7$):

$$H_3C_6H_5O_7 + 3NaHCO_3 \rightarrow Na_3C_6H_5O_7 + 3CO_2 + 3H_2O \tag{6.94}$$

Citric acid ($H_3C_6H_5O_7$) is dissolved in water; this reaction is endothermic, letting the temperature of the solution drop noticeably. If we wait long enough, we can start with this solution at room temperature. The solution is poured into a small glass and placed on top of a scale; a temperature probe is put in the liquid. Then sodium bicarbonate ($NaHCO_3$) is added. Sodium citrate ($Na_3C_6H_5O_7$), water and carbon dioxide are produced in the reaction, leading to fizzing which generates a lot of foam.

Observations. The carbon dioxide that is produced escapes, making the mass of the solution decrease, and the temperature drops. These are the most easily observed effects (Fig. 6.43). The temperature drops by more than 10°C and then slowly recovers. The drop is due to the endothermic effect of the reaction, the recovery is caused by entropy flowing from the environment into the cold solution. The decrease of mass is a little less than 4 g. The scale was zeroed before the bicarbonate was added, so the jump of 8 g represents the mass of bicarbonate added to the citric acid solution. The decease is caused by the carbon dioxide escaping. In fact, the quantities of citric acid and bicarbonate are such that all of the latter should be used up; this is indeed the case.

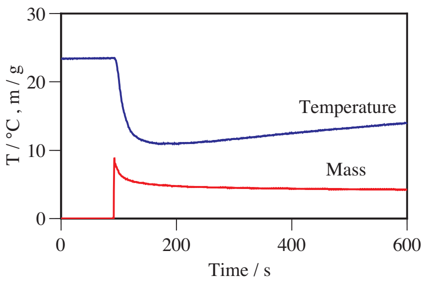


Figure 6.43: Data of temperature and mass of a solution of citric acid (6.82 g) in 23.7 g of water with 8 g of sodium bicarbonate added. It turns out that all of the bicarbonate is used up in the reaction.

Model of the reaction. We need to express the laws of balance of the five substances involved in the reaction of Equ.(6.94) (this was already done in Example 6.3). Each one involves the reaction rate of one of the species. Since the reaction rates are related by Equ.(6.19), only one of them has to be expressed by a constitutive law similar to Equ.(6.93). We do not have to go through the details of the algebra since it works out similarly to what we have done twice already. First, we note that bicarbonate appears with a stoichiometric coefficient of 3 in the reaction equation. This is equal to having the substance $NaHCO_3$ appearing three times, like three different substances. Therefore, the product of concentrations multiplying the chemical driving force (see Equ.(6.92)) will involve the concentration of citric acid and the concentration of bicarbonate raised to the third power. Let us further assume that the reaction proceeds pretty much all the way from left to right in Equ.(6.94), meaning that at least one of the reactants will be used up completely (a simple calculation of the balance of mass of the reaction—the change of mass must be equal to the mass of the carbon dioxide that is produced and escapes—shows that the assumption is reasonable). Put differently, the equilibrium constant of this reaction must be very large. Combining these observations and assumptions leads to an expression of the form

$$\Pi_{n,\mathrm{CA}} = -V k \bar{c}_{\mathrm{CA}} \bar{c}_{BC}^{3} \tag{6.95}$$

The reaction rate for sodium bicarbonate is three time the value of Equ.(6.95), and those of the three products are obtained similarly. If we assume that the escape of CO_2 is responsible for the change of mass, i.e.,

$$\frac{dm}{dt} = -M_{0,\mathrm{CO2}} \Pi_{n,\mathrm{CO2}}$$

we can use data obtained in the experiment to determine whether or not the expression for the reaction rate(s) Equ.(6.95) works out (Fig. 6.44). For the particular case reported here, the exponent of the concentration of bicarbonate is 2.5 rather than 3. Real cases are not always follow the simplest suggestions.

Balance of entropy. Why does the temperature drop? We can answer this question by considering the balance of entropy of the substances involved. Apart from the five reacting substances, there is water. We can assume the temperature measured in the experiment (Fig. 6.43) to be that of the water which allows us to work out the balance of entropy for this substance (Fig. 6.45). We look at the water as the substance which relates what is happening to the reacting substances. Entropy produced in the reaction ($\Pi_{S,reaction}$) is added to the water and so is the entropy given up by the reactants which disappear ($I_{S,R}$). The products receive the entropy they contain from the water ($I_{S,P}$). Finally, the liquid receives entropy from the glass container ($I_{S,gw}$) and indirectly from the environment ($I_{S,env}$). Since $S_{total} = S_{water} + S_{chemicals}$, and

$$\frac{dS_{total}}{dt} = I_{S,gw} + \Pi_{S,reaction}$$

we can formally write the rate of change of entropy of the water as

$$\frac{dS_{water}}{dt} = k_S A\left(T_g - T_w\right) + \frac{1}{T}\frac{1}{\nu_{\mathrm{CA}}}\left[\Delta\mu\right]_{Reaction}\Pi_{n,\mathrm{CA}}$$
$$-\left[-\left(3\bar{s}_{\mathrm{CO2}} + 3\bar{s}_{\mathrm{H2O}} + \bar{s}_{\mathrm{SC}}\right) + \left(3\bar{s}_{\mathrm{BC}} + \bar{s}_{\mathrm{CA}}\right)\right]\Pi_{n,\mathrm{CA}}$$

The last term is the rate of change of entropy of the reacting species. There is a small increase in the amount of water due to the reaction; however, this will be neglected in the model.

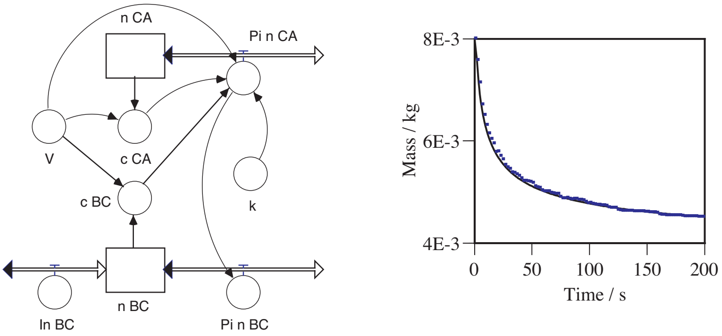
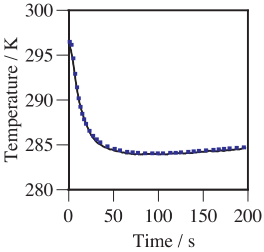


Figure 6.44: Part of the diagram of a system dynamics model of the reactions (left; compare to Example 6.3). The reaction rate of citric acid (CA) involves its concentration and that of bicarbonate (BC). Right: Comparison of simulation results for the mass of the solution with data. The best fit was obtained for c_BC raised to a power of 2.5.

The practical problem consists of finding missing property values, chief among them the difference of chemical potentials of the reaction and the molar entropies of the substances. Molar entropies of CO_2, water, and bicarbonate are 213 J/(K·mole), 69.9 J/(K · mole), and 102 J/(K · mole), respectively. Those of citric acid and sodium citrate could not be found. Fortunately, if the temperature does not vary too much, these unknown contributions are proportional to the contribution of the unknown chemical potential difference. So we basically have to determine one unknown parameter

$$\frac{1}{T}\left[\Delta\mu\right]_{Reaction} - \bar{s}_{\mathrm{CA}} + \bar{s}_{\mathrm{SC}}$$

apart from those governing entropy transfer from the air to the glass container, and from the container to the water. In the model in Fig. 6.45, the difference of the molar entropies of citric acid and sodium citrate has been set equal to zero. With these assumptions, the model yields a rather good fit between simulated and measured values (see the graph in Fig. 6.45), for $[\Delta\mu]_R = -98$ kG.



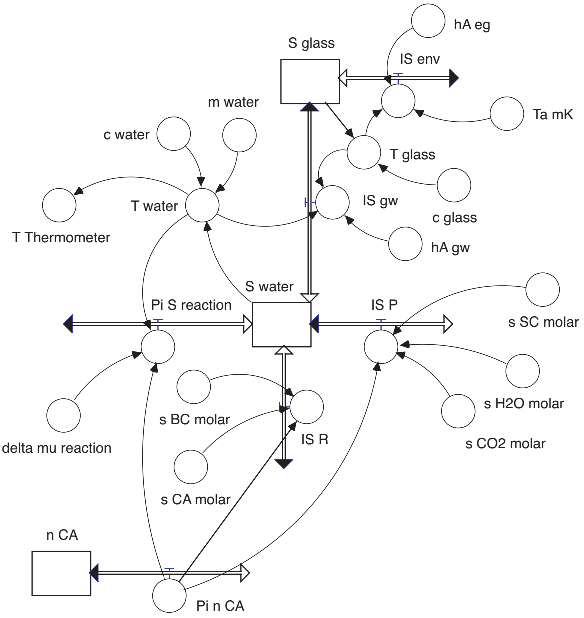


Figure 6.45: Thermal part of a system dynamics model of the reaction of citric acid (CA) and bicarbonate (BC) forming water, CO_2, and sodium citrate (SC). The balance of entropy is expressed for the water whose temperature is measured (entropy production due to transfer from the glass to the water has been neglected). Top: Comparison of data and simulation.

6.8.5 Radioactive Decay

Now we can understand the well known form of the decay rate of radioactive decay that leads to exponential decrease of an unstable isotope:

$$\Pi_{n,radioactive} = -\lambda n \tag{6.96}$$

Here, n is the amount of substance of the radioactive species, and λ is the decay constant. If we start with Equ.(6.83) and accept what is known from nuclear physics, namely, that the chemical driving force of the decay of A into B is (virtually) constant, we arrive at

$$\Pi_{n,radioactive} = V k' \bar{c}_A \Delta\mu_{A\rightarrow B} = -kV\bar{c}_A$$

which is equivalent to Equ.(6.96). The reason for the constancy of the chemical driving force is that it depends upon the (molar) energy released which is the large nuclear part plus negligibly small contributions from chemical and thermal factors such concentration and temperature.

6.8.6 Equilibrium in Chemical Reactions

Let us now turn to the derivation of a more general expression of the condition of chemical equilibrium. Normally, this is done in terms of quantities related to standard values of pressure, temperature, and concentration, rather than the equilibrium values used in Equ.(6.91). This will allow us to obtain a second meaning of the equilibrium constant in terms of the chemical driving force at standard values. For the following, let me write a general reaction equation in the form:

$$0 = a\mathrm{A} + b\mathrm{B} + \ldots + c\mathrm{C} + d\mathrm{D} + \ldots \tag{6.97}$$

A, B… are assumed to be used up, whereas C, D… are produced. We give the first coefficients *a*, *b*, … negative values, while the *c*, *d*, … are taken to be positive:

$$a, b, \ldots < 0 \quad , \quad c, d, \ldots > 0$$

Equilibrium concentrations for ideal gases and dilute solutions. To find the actual composition of the substances after equilibrium has been reached, we must express the chemical potential of each species involved in terms of the actual temperature and pressure (or concentration). If we assume that equilibrium has been achieved at standard conditions for the mixture, only the partial pressure (concentration) of a species is different from P_0; the temperature takes the standard value of 298 K. For the case of a mixture of ideal gases, the chemical potentials depend upon pressure as follows (Equ.(6.46)):

$$\mu_i = \mu^0 + RT \ln\left(\frac{P_i}{P_0}\right) \tag{6.98}$$

The index 0 refers to the standard state. For dilute solutions, the partial pressure can be replaced by the concentration according to Equ.(6.60):

$$P_i = RT\,\bar{c}_i \tag{6.99}$$

where you have to remember that the standard concentration for the calculation of the standard values of the chemical potential is 1 mole/liter, and not 1 mole/m^3. The expression of the chemical potential is the same for dilute solutions and ideal gases. If we introduce Equ.(6.98) in the condition of equilibrium, we obtain

$$0 = \sum_{species} v_i\left[\mu_i^0 + RT \ln\left(\frac{P_i^{eq}}{P_0}\right)\right] = \sum_{species} v_i\mu_i^0 + \sum_{species} v_i RT \ln\left(\frac{P_i^{eq}}{P_0}\right)$$

The first term on the right is the change of the chemical potential for the reaction at standard conditions; if we also rewrite the second term, the condition reads

$$0 = \left[\Delta\mu^0\right]_{reaction} + RT \ln\left(\frac{\left(P_a^{eq}\right)^a}{\left(P_0\right)^a}\frac{\left(P_b^{eq}\right)^b}{\left(P_0\right)^b}\cdots\frac{\left(P_c^{eq}\right)^c}{\left(P_0\right)^c}\frac{\left(P_d^{eq}\right)^d}{\left(P_0\right)^d}\cdots\right) \tag{6.100}$$

Remember to use the proper sign of the stoichiometric coefficients *a*, *b*,…as defined above. It is customary to call the quantity in parenthesis the equilibrium constant $\mathcal{K}_P$:

$$\mathcal{K}_P \equiv \frac{\left(P_a^{eq}\right)^a}{\left(P_0\right)^a}\frac{\left(P_b^{eq}\right)^b}{\left(P_0\right)^b}\cdots\frac{\left(P_c^{eq}\right)^c}{\left(P_0\right)^c}\frac{\left(P_d^{eq}\right)^d}{\left(P_0\right)^d}\cdots \tag{6.101}$$

The index *P* refers to pressure. Note that the stoichiometric coefficients appear as exponents. In general, they do not balance so that the standard pressure would drop out of this expression. Therefore, the equilibrium constants in Equ.(6.74), Equ.(6.86), and Equ.(6.91) are special results. With the general definition of the equilibrium constant, the condition of chemical equilibrium in a mixture of ideal gases can be written in the following simple form:

$$RT\ \ln\left(\mathcal{K}_P\right) = -\left[\Delta\mu^0\right]_{reaction} \tag{6.102}$$

The equilibrium constant has a value which is independent of pressure (since the right-hand side of the equation has been defined for the fixed standard pressure); i.e., it only depends upon the temperature. With the known change of chemical potential for the reaction for standard conditions, $\mathcal{K}_P$ can be calculated; this then yields the relation between the partial pressures or concentrations of the species taking part in the reaction.

As we have seen before, changing the temperature at which the reaction takes place can influence the outcome, i.e., the equilibrium concentrations of the substances. The same is true of a change of pressure. Even though the equilibrium constant is independent of pressure, the values of the partial pressures will change. Therefore, with changes both of temperature and of pressure, the outcome of a reaction can be shifted to favor one side.

Chemical equilibria do not occur only in outright chemical reactions. As we have seen already, the concept of equilibrium can be applied to such diverse situations as the vapor pressure of a liquid, the condensation of vapor, the solution of gases in water, and more. In particular, Equ.(6.102) can also be applied to the transport of substances discussed before in Section 6.7.3.

QUESTIONS

41. In what sense are the transport of a substance from one environment into another chemically different one and the transformation of a substance A into B comparable?
42. If standard reasoning were to apply, what would the order of the reaction rate for the conversion of hydrogen and oxygen to water be?
43. The reaction described in Equ.(6.88) is said to be of first order. If $\mathcal{K}$ is large, what kind of function of time is the concentration of the reacting substance expected to be?
44. Assume a substance A to react with a substance B according to A + B = C. If there is a great excess of amount of B in the reacting mixture, why does the reaction behave like one of the first order?
45. Why do the results of experiment and models reported in Fig. 6.42 tell us that the reaction rate probably does not depend linearly upon the chemical driving force?
46. What does it mean when the equilibrium constant is small? Large? Equal to 1? Do you know of a process where $\mathcal{K} = 1$?
47. For the conversion of α-glucose into β-glucose, $\mathcal{K} = 1.77$. How large is the standard difference of chemical potentials of this conversion?

EXAMPLE 6.22. Synthesizing hydrogen iodide.

Hydrogen iodide HI which is used to primarily in the manufacture of hydriodic acid and in the preparation of organic and inorganic iodides is synthesized by the reaction $H_2 + I_2 \rightarrow 2HI$.

Thermochemical data for the substances involved are reported in the table below. For a temperature of 400 K, the kinetics of the reaction has been given as[11]:

$$\frac{d\bar{c}_{\mathrm{HI}}}{dt} = k_1 \bar{c}_{\mathrm{H2}}\bar{c}_{\mathrm{I2}} - k_2\left(\bar{c}_{\mathrm{HI}}\right)^2$$

$$k_1 = 6.3\cdot 10^{-8}\,\frac{\mathrm{cm}^3}{\mathrm{mole}\cdot\mathrm{s}} \quad , \quad k_2 = 8.0\cdot 10^{-11}\,\frac{\mathrm{cm}^3}{\mathrm{mole}\cdot\mathrm{s}}$$

Table 6.9: Hydrogen, iodine, and hydrogen iodide

	μ / kG	α / G/K
H_2 (gas)	0	– 130.58
I_2 (gas)	19.37	– 260.58
HI (gas)	1.3	– 206.5

(a) Write the kinetic equation for H_2 in the standard form (see Equ.(6.93)). Determine the rate constant k in standard units (volume in m^3). What is the equilibrium constant according to this equation? (b) Calculate the equilibrium constant from the values in the table and compare to the result found in (a). (c) Assume the volume of the reactor to be 100 L and initial concentrations of H_2 and I_2 of 10 kmole/m^3 each (there is no HI present). What are the initial rates of change of concentrations? (d) Sketch the amounts of substance of H_2, I_2, HI as functions of time.

SOLUTION: (a) The standard form turns out to be

$$\frac{dn_{\mathrm{H2}}}{dt} = V\,k\left(\left(\bar{c}_{\mathrm{HI}}\right)^2 - \mathcal{K}\bar{c}_{\mathrm{H2}}\bar{c}_{\mathrm{I2}}\right)$$

with $k = 4.0\cdot 10^{-17}$ m^3/(mole·s) and $\mathcal{K} = 788$.

(b) The chemical potentials appearing in the expression of chemical equilibrium must be calculated for the actual conditions (actual pressures or concentrations and temperature):

$$\mu_{H2}\left(T, P_{\mathrm{H2}}^{eq}\right) + \mu_{I2}\left(T, P_{\mathrm{I2}}^{eq}\right) = 2\mu_{HI}\left(T, P_{\mathrm{HI}}^{eq}\right)$$

$$\mu_{\mathrm{H2}}\left(T_0, P_{\mathrm{H2}}^0\right) + RT\ln\left(\frac{P_{\mathrm{H2}}^{eq}}{P_{\mathrm{H2}}^0}\right) + \alpha_{\mu,\mathrm{H2}}\left(T - T_0\right) + \mu_{\mathrm{I2}}\left(T_0, P_{\mathrm{I2}}^0\right) + RT\ln\left(\frac{P_{\mathrm{I2}}^{eq}}{P_{\mathrm{I2}}^0}\right) + \alpha_{\mu,\mathrm{I2}}\left(T - T_0\right)$$

$$= 2\mu_{\mathrm{HI}}\left(T_0, P_{\mathrm{HI}}^0\right) + 2RT\ln\left(\frac{P_{\mathrm{HI}}^{eq}}{P_{\mathrm{HI}}^0}\right) + 2\alpha_{\mu,\mathrm{HI}}\left(T - T_0\right)$$

With $T = 400$ K, we have

$$RT\ln\left(\left(\frac{P_{\mathrm{HI}}^{eq}}{P_{\mathrm{HI}}^0}\right)^2\left(\frac{P_{\mathrm{H2}}^{eq}}{P_{\mathrm{H2}}^0}\right)^{-1}\left(\frac{P_{\mathrm{I2}}^{eq}}{P_{\mathrm{I2}}^0}\right)^{-1}\right)$$

$$= -\left(-\mu_{\mathrm{H2}}\left(T_0, \bar{c}_{\mathrm{H2}}^0\right) - \mu_{\mathrm{I2}}\left(T_0, \bar{c}_{\mathrm{I2}}^0\right) + 2\mu_{\mathrm{HI}}\left(T_0, \bar{c}_{\mathrm{HI}}^0\right)\right) + \left(T - T_0\right)\left[\alpha_{\mu,\mathrm{H2}} + \alpha_{\mu,\mathrm{I2}} - 2\alpha_{\mu,\mathrm{HI}}\right]$$

and

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[11] Rosenqvist T. (2004): Principles Of Extractive Metallurgy. p.132.

$$\mathcal{K}_P = \frac{\left(P_{\mathrm{HI}}^{eq}\right)^2}{P_{\mathrm{H2}}^{eq} P_{\mathrm{I2}}^{eq}} = \exp\left[\frac{-\left[2\cdot 1300-(0+19370)\right]+(400-298)\left[-130.58-260.58+2\cdot 206.5\right]}{8.314\cdot 400}\right]$$

$$= \exp(5.71) = 302$$

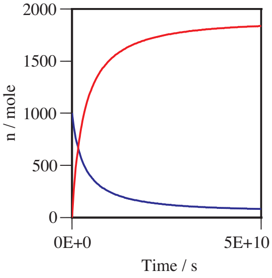

Figure Ex.22

This is smaller by more than a factor of 2 than the constant assumed in the actual kinetics reported above.

(c). The rate of change of amount of substance divided by the volume of the reactor equals the rate of change of concentration. Inserting numbers in the expression given in (a) yields a value of $-3.15\cdot 10^{-7}$ mole/(s·m^3) for H_2 and I_2. The rate of change for HI is $6.3\cdot 10^{-7}$ mole/(s·m^3).

(d) Equilibrium values and initial rates allow us to sketch the amounts of substance as functions of time (Fig. Ex.22), so we still need the equilibrium amounts for the three species. The expression for the equilibrium constant can be written with the concentrations which can be converted to amount of substance:

$$\mathcal{K}_c = \frac{\left(P_{\mathrm{HI}}^{eq}\right)^2}{P_{\mathrm{H2}}^{eq} P_{\mathrm{I2}}^{eq}} = \frac{\left(\bar{c}_{\mathrm{HI}}^{eq}\right)^2}{\bar{c}_{\mathrm{H2}}^{eq}\bar{c}_{\mathrm{I2}}^{eq}} = \frac{\left(n_{\mathrm{HI}}^{eq}\right)^2}{n_{\mathrm{H2}}^{eq} n_{\mathrm{I2}}^{eq}} = \frac{\left(2n_{\mathrm{H2},init} - 2n_{\mathrm{H2}}^{eq}\right)^2}{n_{\mathrm{H2}}^{eq} n_{\mathrm{H2}}^{eq}}$$

The last step involves the observations that n_{I2} must be equal to n_{H2}, and that n_{HI} is calculated from the total amounts (at the beginning) and the final quantities of the reactants. The solution of this quadratic equation is

$$n_{\mathrm{H2}}^{eq} = n_{\mathrm{I2}}^{eq} = 66.5\,\mathrm{mole} \quad , \quad n_{\mathrm{H2}}^{eq} = 2000\,\mathrm{mole} - 2\cdot 66.5\,\mathrm{mole} = 1867\,\mathrm{mole}$$

6.9 CARBON DIOXIDE IN THE ATMOSPHERE AND OCEANS

We strongly suspect that human generation of carbon dioxide in the burning of fossil fuels and deforestation is responsible for changing the chemistry of the atmosphere to such an extent that our climate will change as well. For this reason, the issue of the global carbon cycle has become pressing. What happens to carbon—in its many combinations—in the biosphere, geosphere, the oceans, and the atmosphere? Where does the CO_2 released by human activity end up?

In this section, I would like to construct a couple of strongly simplified models of the exchange of CO_2 between atmosphere and oceans, and reactions of CO_2 in sea water. The models can only suggest the ideas involved in research concerning the carbon cycle—they should not be regarded as furnishing realistic numbers. Rather, they provide a nice application of the physics we have been studying in this chapter.

There are two important time series concerning the phenomenon: The rate of production of CO_2 by human activity (Fig. 6.46, left), and the concentration of CO_2 in the atmosphere (Fig. 6.46, right). The former has been compiled from data on economic activity,[12] the latter stems from measurements. There is ice core data for the time from 1750 until the onset of detailed and careful measurements of atmospheric CO_2 on Mauna Loa in Hawaii at about 1960.[13]

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[12] Marland G., Boden T. A., Andres R. J.: Global, regional, and national fossil fuel CO2 emissions. cdiac.ornl.gov/trends/emis/em_cont.html.

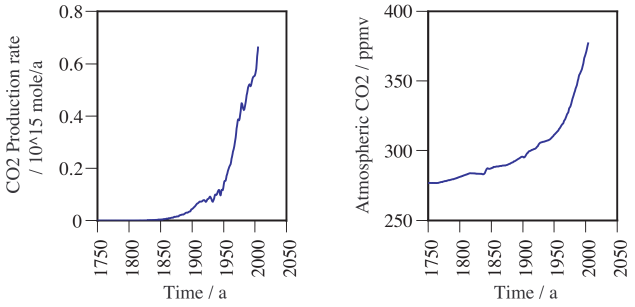

Figure 6.46: Left: CO_2 emissions by fossil fuel burning, in Pmole/a (10^{15} mole/a). Right: Concentration of CO_2 in the atmosphere from ice core data and directly from the atmosphere (Mauna Loa data). ppmv denotes parts per million by volume.

6.9.1 Exchange of Carbon Dioxide Between Air and Water

What I have called spatially uniform models of elements of larger systems are often termed box models in the research community. Such models—when detailed enough—provide much insight into the phenomena surrounding carbon in general and CO_2 in the atmosphere in particular.[14] Here, I would like to present the simplest possible two-box model (Fig. 6.47) involving carbon dioxide in the atmosphere and the oceans using the ideas of chemical driving forces, flows, and balances of amounts of substances.

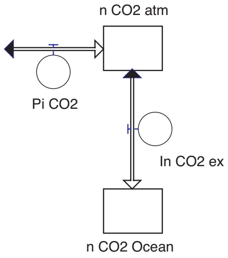

Figure 6.47: In this two-box model, carbon dioxide resides in the atmosphere and in the ocean water. CO_2 is added to the atmosphere as a result of human activity, and it is exchanged between air and water.

The input (Pi_CO2) in the model of Fig. 6.47 stems from carbon dioxide production according to Fig. 6.46 (left). The flow between atmosphere and ocean can be modeled along the lines of Section 6.7.3.

For the following discussions, let us assume that we do not have to consider temperature (changes); in other words, take the temperature to be 298 K for all relevant components. Similar to the example of humidity in the air (Example 6.16), we consider the chemical driving force between CO_2 in the air and CO_2 dissolved in water:

$$\Delta\mu = \mu_{CO2(aq)}\left(T_0, \bar{c}_{CO2(aq)}\right) - \mu_{CO2(gas)}\left(T_0, P_{CO2(gas)}\right) \tag{6.103}$$

The chemical potential of CO_2 in water is determined by its concentration. In the air, it is determined by its partial pressure:

$$\begin{aligned}\Delta\mu = {} & \mu_{CO2(aq)}\left(T_0, \bar{c}^{\,0}_{CO2(aq)}\right) + RT\,\ln\left(\frac{\bar{c}_{CO2(aq)}}{\bar{c}^{\,0}_{CO2(aq)}}\right) \\ & - \left[\mu_{CO2(gas)}\left(T_0, P_0\right) + RT\,\ln\left(\frac{P_{CO2(gas)}}{P_0}\right)\right]\end{aligned} \tag{6.104}$$

---

13. Siple Station data: Neftel A., Friedli H., Moor E., Lötscher H., Oeschger H., Siegenthaler U., Stauffer B.: Historical Carbon Dioxide Record from the Siple Station Ice Core. cdiac.ornl.gov/trends/co2/siple.html. Mauna Loa data: Ralph Keeling, (Scripps Institution of Oceanography, University of California, San Diego): Atmospheric Carbon Dioxide – Mauna Loa. www.esrl.noaa.gov/gmd/ccgg/trends/co2_data_mlo.html

[14] See Tomizuka A. (2009) for a discussion of a seven-box model.

We need to know the partial pressure of CO_2 in the atmosphere. For ideal gases, the fraction of volume taken by a component is also the fraction of the total pressure. So, the partial pressure of CO_2 in the air is $280 \cdot 10^{-6} \cdot 10^5$ Pa = 28 Pa for the preindustrial level (38 Pa for modern levels, see Fig. 6.46, right). The current of CO_2 between atmosphere and ocean can be calculated according to Equ.(6.71) (the partial pressure of carbon dioxide in the atmosphere can be converted to concentration by dividing by RT):

$$I_{n,CO2} = k_1 P_{CO2,atm} \Delta\mu \tag{6.105}$$

Here, I have included the surface area (contact area between atmosphere and oceans) in the transport coefficient k_1. All of this can be added to the structure of laws of balance in Fig. 6.47 to yield a model diagram as in Fig. 6.48 (left).

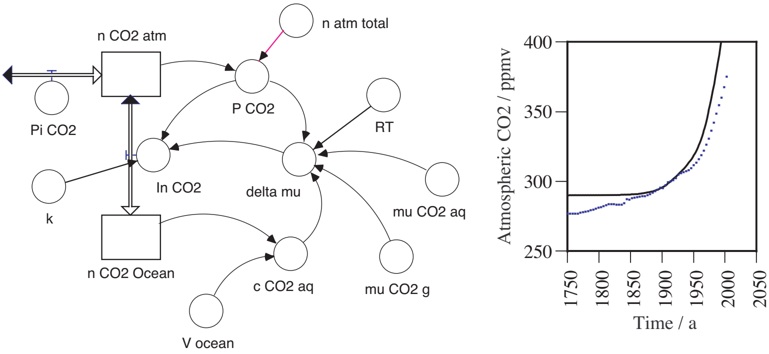

Figure 6.48: Diagram of system dynamics model of CO_2 exchange between atmosphere and ocean (left). The simulation shows atmospheric concentrations of CO_2 (dots: data; solid line: simulation).

The total amount of substance in the atmosphere and the relevant volume of the ocean can be found as follows. The mass of the atmosphere can be calculated from the pressure it exerts upon the surface of the planet; pressure multiplied by surface area yields the weight of the atmosphere which is converted to mass which is converted to amount of substance (assuming an average molar mass of 0.029 kg/mole). The result is roughly $1.8 \cdot 10^{20}$ mole. Determining the volume of water relevant for this strongly limited model is a little more uncertain. It makes sense to use only the upper parts of the oceans that are mixing quickly (mixing layer). This mixing layer is assumed to be a spatially uniform repository for CO_2. It has variable thickness, typically between 50 m and 200 m. I will take a layer of 150 m covering 70% of the surface of the planet. The resulting volume is $54 \cdot 10^{15}$ m^3.

All we still need are initial values for CO_2 in the two reservoirs. I chose 290 ppmv for the atmospheric level in 1750, slightly up from the value reported from ice core data (277 ppmv). The elevated value makes the simulation (Fig. 6.48, left) coincide with actual values somewhere between 1850 and 1900 when generation of CO_2 by fossil fuel burning started to make a difference (Fig. 6.46, left). This means that the rise in atmospheric carbon dioxide before 1850 seen in the ice core data cannot stem from our consumption of fuels.

The second initial value is for the amount of carbon dioxide dissolved in the upper 150 m of the oceans. I chose a value of close to 0.010 mole/m^3 which stems from applying Equ.(6.104) to the steady-state (see Example 6.23). In other words, I assume that in preindustrial times, CO_2 in the atmosphere and in the water was in equilibrium.

The result of a simulation of this model is found in the graph of Fig. 6.48 (right, solid line). Actually, there are two solid lines coinciding in the graph: Simulated CO_2 in the atmosphere, and the values obtained by adding all the CO_2 produced from fossil fuel burning to the original 290 ppmv. This simply means that in our model, virtually all the carbon dioxide produced by human activity ends up in the atmosphere, making the calculated levels noticeably higher than the actual ones (dots in the graph of Fig. 6.48).

6.9.2 The Chemistry of Sea Water

Why doesn't the ocean in our model absorb (much of) the carbon dioxide released into the atmosphere? Actually, it takes up as much as the assumptions allow. The concentration rises from 0.010 mole/m^3 to 0.015 mole/m^3 which corresponds to the fractional increase of the simulated concentration in the atmosphere. The result simply confirms Henry's law (Example 6.19).

In reality, water takes up a lot more carbon dioxide than our model can explain. Reported solubilities of CO_2 in sea water are about 2 mole/m^3, roughly two hundred times higher than what we calculate from Equ.(6.104) and data in Table 6.4. How can this be explained?

The reason is conceptually simple but intricate in detail. It has to do with CO_2 reacting in water in a way that removes much of the dissolved gas, allowing more carbon dioxide from the atmosphere to enter the ocean.[15] Carbon dioxide always reacts with water to form carbonic acid (H_2CO_3) which forms bicarbonate ions ($HCO_3{}^-$) which form carbonate ions ($CO_3{}^{2-}$):

$$\mathrm{CO_2}(aq) + \mathrm{H_2O} \Leftrightarrow \mathrm{H_2CO_3} \Leftrightarrow \mathrm{H^+} + \mathrm{HCO_3^-} \Leftrightarrow 2\mathrm{H^+} + \mathrm{CO_3^{2-}} \qquad \textbf{(6.106)}$$

Sea water adds components such as biological activity and alcalinity to this picture that make details even more complex.

We should try to understand the formation of carbonates in fresh water to get a feeling for the most important aspects of the chemistry of CO_2 in water. One of the questions we can answer directly concerns equilibrium concentrations of the species involved in the chain of reactions in Equ.(6.106). According to Section 6.8.6, we can define the equilibrium constants of the three reactions in terms of the concentrations of the six substances H_2O, CO_2, H_2CO_3, $HCO_3{}^-$, $CO_3{}^{2-}$, and H^+:

$$\mathcal{K}_1 = \frac{\overline{c}_{\mathrm{H2CO3}(aq)}}{\overline{c}_{\mathrm{CO2}(aq)}\overline{c}_{\mathrm{H2O}}} \quad , \quad \mathcal{K}_2 = \frac{\overline{c}_{\mathrm{H+}(aq)}\overline{c}_{\mathrm{HCO3^-}(aq)}}{\overline{c}_{\mathrm{H2CO3}(aq)}} \quad , \quad \mathcal{K}_3 = \frac{\overline{c}_{\mathrm{H+}(aq)}\overline{c}_{\mathrm{CO3^{2-}}(aq)}}{\overline{c}_{\mathrm{HCO3^-}(aq)}} \qquad \textbf{(6.107)}$$

Standard concentrations drop out of these relations if we choose them to be 1 mole/L.

On the other hand, the equilibrium constants can be calculated with the help of Equ.(6.102) using the standard chemical potentials which are listed in Table 6.10. These provide three more conditions for the nine unknowns (three constants and six

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[15] For a discussion of the interaction of atmosphere and ocean, see Feely R. A., Sabine C. L., Takahashi T., and Wanninkhof R. (2001). David Bice (2001) published extensive resources, including simple dynamical models, online (www.earthscape.org).

Table 6.10: Water chemistry

Formula	Chemical potential/ kJ/mole[a]
H_2O (l)	– 237.18
CO_2 (aq)	– 385.99
H_2CO_3 (aq)	– 608.25
HCO_3^- (aq)	– 586.85
CO_3^{2-} (aq)	– 527.90
H^+ (aq)	0
OH^- (aq)	– 157.29

a. At standard conditions: 298.15 K, 101,325 Pa, pure or 1 mole/l.

concentrations). We need three more relations or conditions. We can specify the concentration of CO_2 by assuming it to be in equilibrium with the gas in the atmosphere; the value is about $1 \cdot 10^{-5}$ mole/L. Furthermore, the concentrations add up to a fixed value which we can take to be the molar concentration of pure water (about 55.5 mole/L):

$$\bar{c}_{\mathrm{H2O}} + \bar{c}_{\mathrm{CO2}(aq)} + \bar{c}_{\mathrm{H2CO3}(aq)} + \bar{c}_{\mathrm{HCO3^-}(aq)} + \bar{c}_{\mathrm{CO3^{2-}}(aq)} + \bar{c}_{\mathrm{H+}(aq)} = \bar{c}_{water} \qquad \textbf{(6.108)}$$

This leaves one condition. Obviously, the concentration of protons (H+) in water plays an important role in the reactions involving carbon dioxide and its derivatives. The concentration of protons is usually given in terms of the pH value of the solution:[16]

$$\mathrm{pH} = -\log_{10}\left(\bar{c}_{\mathrm{H+}(aq)} / \bar{c}_0\right) \qquad \textbf{(6.109)}$$

All unknown concentrations can be calculated by specifying the proton concentration or the pH. It is customary to report the concentrations of CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-} relative to the total concentration of the species containing carbon. Results of these calculations are shown as functions of the pH of the solution in Fig. 6.49. Remember that these results hold for water without additional solutes (apart from what is needed to change the concentration of protons).

For a pH value similar to the one of sea water (slightly more than 8), the numbers shown in Fig. 6.49 indicate that only one in 2500 molecules containing carbon is carbon dioxide. Almost all of the carbon is in bicarbonate ions. Since important other factors influence the equilibria in sea water, the curves shift and change somewhat. The changes are significant for small fractions, so the detailed chemistry of sea water is crucial when it comes to determining more reliable values of CO_2 versus the other inorganic carbon compounds. Results reported by Feely et al.[17] give a ratio of 1 : 200 for $CO_2 : HCO_3^-$, and about 6 : 1 for $HCO_3^- : CO_3^{2-}$ for the mixed upper ocean layer in equilibrium with the atmosphere containing pre-industrial concentrations of CO_2 (some 280 ppmv). As the atmospheric concentration of carbon dioxide increases, the relative amount of dissolved CO_2 (relative to total *Dissolved Inorganic Carbon*, DIC) should increase, and the pH of the oceans should decrease to slightly below 8 (this is considered a significant change of acidity, important for corals and other marine life).

Let me incorporate the results of this section in a second dynamical model in a strongly simplified manner (Fig. 6.50). Clearly, CO_2 that is dissolved in water reacts, i.e., it is destroyed and other dissolved inorganic carbon compounds are produced. A simple idea is to take CO_2 as a species A and lump all other DIC compounds as a single species B. A reacts with water to produce B:

$$\mathrm{CO_2}(aq) + \mathrm{H_2O} \leftrightarrow \mathrm{DIC} \qquad \textbf{(6.110)}$$

---

[16] In pure water, there is a small amount of protons (H^+) and OH^-, the other component of the dissociation of water ($H_2O \leftrightarrow H^+ + OH^-$). In equilibrium, which is determined by the standard values of the chemical potentials of the three species, the concentration of protons is 10^{-7} mole/L which corresponds to a pH of 7.

[17] Feely R. A., Sabine C. L., Takahashi T., and Wanninkhof R. (2001).

In equilibrium, there is a certain small fraction of CO_2 relative to DIC left in the water. We can interpret the deviation from equilibrium as the driving force for the reaction in Equ.(6.110) as we did before:

$$\Pi_{CO2(aq)} = k_2 \bar{c}_{CO2(aq)} \left(\bar{c}_{DIC} - \mathcal{K} \bar{c}_{CO2(aq)} \right) \tag{6.111}$$

$\mathcal{K}$ should take values of the order of 1/200. Adding this reaction to the model discussed in Fig. 6.48 is simple (see Fig. 6.50, left).

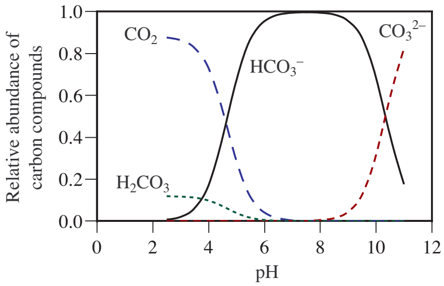

Figure 6.49: Diagram of relative concentrations of CO_2, carbonic acid, bicarbonate and carbonate ions as functions of pH. Sea water has a pH slightly higher than 8. Even though the curves are somewhat different for the conditions in sea water, we can still tell that most of the carbon is in bicarbonate ions (solid line).

There are two more parameters of the model that need to be fixed before we can attempt a simulation. These are the transport coefficient k_1 in Equ.(6.105), and the reaction coefficient k_2 in Equ.(6.111). If we give these factors large values, simulation results (such as the atmospheric carbon dioxide concentration) do not change further, even if the parameters are made larger. What this means is simple: with very large values of process coefficients, the model calculates an evolution that goes through almost perfect equilibrium states. Put differently, a jump in a concentration decays very fast and chemical equilibrium is attained again almost perfectly at every point in time.

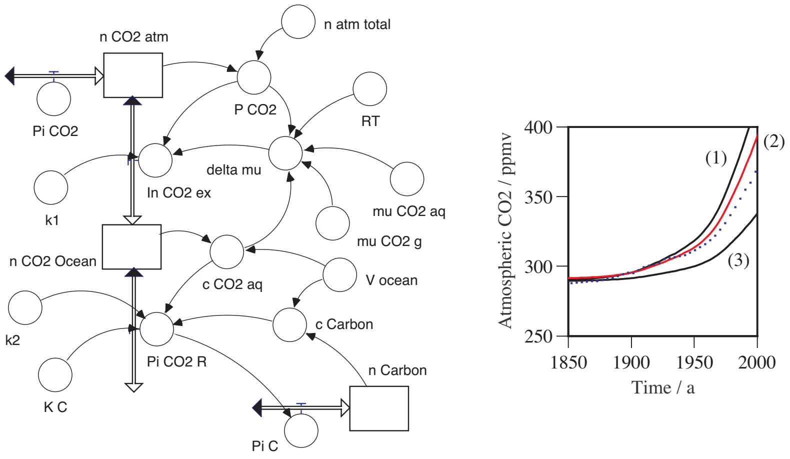

Figure 6.50: Diagram of system dynamics model of CO_2 exchange between atmosphere and ocean, and reactions of CO_2 in water (left). The simulation shows atmospheric concentrations of CO_2 (dots: data; solid lines: simulations). K_C: 0.04 and 0.006 (a fit of data is achieved with 0.015). The results are for high values of transport and reaction constants leading to almost instantaneous equilibria.

When we assume such large values of the transport and reaction coefficients, we obtain the results shown in the graph on the right of Fig. 6.50. The one still uncertain but important parameter is the equilibrium constant $\mathcal{K}$ for the reaction in Equ.(6.111). A value of $\mathcal{K} = 0.04$ predicts atmospheric CO_2 concentrations (solid line (2)) that are higher than the observed concentrations (dots). In fact, the numbers are only slightly below what we get if all the CO_2 emitted by fossil fuel consumption stays in the air (solid line (1)). If we use a value of $\mathcal{K} = 0.006$ (close to what we need if we want dissolved carbon dioxide to be only 1/200 of DIC), we get solid line (3) which is considerably lower than observed values.

How could we find more realistic values of transport and reaction coefficients? A large reaction coefficient k_2 probably makes sense. Once carbon dioxide is dissolved in water, formation of carbonic acid, bicarbonate and carbonate ions proceeds very quickly. However, the case of the transfer coefficient k_1 is different. One might expect the mixing of CO_2 in the air and the oceans to take some time. Imagine a sudden jump in atmospheric carbon dioxide. A time constant of one year for the subsequent adjustment does not seem to be unreasonable. A different piece of information that allows us to estimate the transfer coefficient is the observation that the average difference of partial pressures of CO_2 in the air and in the world's oceans is a little less than 1 Pa.[18] Interestingly, a value of k_1 that yields such a pressure difference in our model of Fig. 6.50 makes the time constant for the exchange of CO_2 roughly one year. Fixing k_1 in this manner and using $\mathcal{K} = 0.005$ leads to carbon dioxide concentrations a little higher than the solid line (3) in the graph of Fig. 6.50 (right).

In summary, aspects of the behavior of carbon dioxide in the atmosphere and oceans can be understood if we create simple dynamical models of chemical processes in analogy to what we have learned in fluids, electricity, and heat. The concepts of quantity and driving force apply to chemical phenomena just as they do to thermal, electrical or fluid processes.

EXAMPLE 6.23. The effect of temperature on the solubility of CO_2.

(a) Calculate the standard value of the concentration of carbon dioxide in water. (The concentration of CO_2 in air is about 350 ppmv.) (b) Determine the effect of changes of temperature upon the solubility. Take the case of arctic waters with a temperature close to 0°C.

SOLUTION: (a) We can directly apply Equ.(6.104) to the first problem. The concentration of CO_2 is proportional to its partial pressure, which means that $P_{CO2}/P_0 = 3.5 \cdot 10^{-4}$. Therefore,

$$\frac{\bar{c}_{aq}}{\bar{c}_0} = \exp\left[\frac{\mu^0_{CO2(gas)} - \mu^0_{CO2(aq)}}{RT} + \ln\left(\frac{P_{CO2(gas)}}{P_0}\right)\right] = 1.18 \cdot 10^{-5}$$

(b) The effect of temperature can be taken into account via the chemical potentials. Since the major contribution comes from the molar entropy, we can write

$$\mu^0_{CO2(gas)} + RT\ln\left(\frac{P_{CO2(gas)}}{P_0}\right) - \Delta T\,\bar{s}_{CO2(gas)} = \mu^0_{CO2(aq)} + RT\ln\left(\frac{\bar{c}_{CO2(aq)}}{\bar{c}_0}\right) - \Delta T\,\bar{s}_{CO2(aq)}$$

Solving this condition for the concentration of the dissolved gas yields

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[18] Feely R. A., Sabine C. L., Takahashi T., and Wanninkhof R. (2001).

$$
\begin{aligned}
\frac{\bar{c}_{CO2(aq)}}{\bar{c}_0} &= \exp\left[\frac{\mu^0_{CO2(gas)} - \mu^0_{CO2(aq)} - \left(\bar{s}_{CO2(gas)} - \bar{s}_{CO2(aq)}\right)\Delta T}{RT} + \ln\left(\frac{P_{CO2(gas)}}{P_0}\right)\right] \\
&= \exp\left[\frac{\mu^0_{CO2(gas)} - \mu^0_{CO2(aq)}}{RT} + \ln\left(\frac{P_{CO2(gas)}}{P_0}\right)\right]\exp\left(-\frac{\left(\bar{s}_{CO2(gas)} - \bar{s}_{CO2(aq)}\right)\Delta T}{RT}\right) \\
&= \exp\left[\frac{-394400 + 385990}{8.314\cdot 298} + \ln\left(3.5\cdot 10^{-4}\right)\right]\exp\left(-\frac{(213.68 - 113.0)(-25)}{8.314\cdot 298}\right) \\
&= \exp(-11.35)\cdot\exp(1.016) = 1.18\cdot 10^{-5}\cdot 2.76 = 3.26\cdot 10^{-5}
\end{aligned}
$$

which corresponds to an increase by a factor of almost 3 in solubility for a decrease in temperature of 25°C. So there is a huge difference in the ability to take up CO_2 in oceans near the equator compared to arctic waters.

EXERCISES AND PROBLEMS

1. (a) Calculate the masses of 1 mole of neon gas, oxygen gas, table salt, glucose. (b) If 10 g of table salt are dissolved in water, how many particles do we get in the solution? (c) The molar mass of water is 0.018 kg/mole. What is the molar volume of water? (d) Sea water has a concentration of salt of about 35 parts per thousand. How many moles of salt is this per liter of water?
2. Sugar is added to a bioreactor at a rate of 2 mole/min. It accumulates at a rate of 0.70 moles/minute. What is the rate of production or consumption of sugar?
3. 5.0 g of glucose are dissolved in 2.0 liters of water. What is the concentration (molar concentration) of the solution?
4. What is the chemical potential difference of the reaction of carbon and oxygen forming carbon dioxide?
5. (a) By how much does the chemical potential of air change if its pressure is raised by a factor of 10? (b) By how much does the chemical potential of dissolved salt change if it is diluted by a factor of 10?
6. Calculate the chemical potential of H_2O in its gaseous, liquid, and solid forms each at temperatures of 200 K, 300 K, and 400 K. From the results deduce which of the forms should be stable at the three temperatures listed.
7. Fast melting of snow (spring runoff) is thought not to be so much a result of warm rain but rather of fog flowing over snow covered slopes. Why should fog be much more effective in melting snow than warm rain? Show that the relation between the mass of snow (modeled as ice) melting and the mass of water vapor condensing out of fog is given by

   $$m_{snow} = 7.5 m_{vapor}$$

   while the ratio of snow melting from condensation of fog and from cooling of rain from temperature T to T_{snow} is roughly $600/(T - T_{snow})$.[19]
8. Consider the conversion of α-glucose into β-glucose (see Fig. 6.3). (a) Determine the equilibrium constant. (b) What is the difference of the chemical potentials at standard conditions?

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[19] See Bohren (1995), p. 79–81.

9. Methane and oxygen gas burn to form carbon dioxide and water. Assume for the following balances that initial substances and products are all at their standard states. Values of chemical potentials and molar entropies are found in tables. (a) What is the chemical reaction formula? (b) Determine the entropy produced per mole of methane. (c) Determine the change of entropy in going from the initial substances to the products (per mole of methane). (d) How much entropy is emitted to or absorbed from the environment (per mole of methane)? (e) How much energy is transferred together with the entropy exchanged? (f) How much energy is this per kilogram of methane? Compare this result to the higher heating value in Table 6.5.

10. Calculate the energy released if one nucleus of ^{90}Sr spontaneously decays into ^{90}Y.

11. The voltage measured for an electrochemical cell (a fuel cell) converting hydrogen and oxygen into water has a maximum value of 1.23 V at standard conditions. Determine the chemical potential of water.

12. By how much does the pressure of water change if we dissolve 0.010 mole of table salt in 1.0 liter of water?

13. Partial pressure of a dissolved gas. It is customary to introduce the "partial pressure" of a dissolved gas as another measure of its concentration. The partial pressure of the dissolved gas is defined as its partial pressure in an atmosphere in equilibrium with the liquid. What is the partial pressure P_{CO2} of carbon dioxide in water having a concentration of 0.020 mole/m^3?

14. At standard conditions, water vapor is present in air at a partial pressure of 30 mbar. How much hydrogen gas will be present relative to the amount of water?

15. In biology, the equilibrium ratio of a substance in two different environments is called the partition coefficient. Determine the partition coefficient for toluene in water and air.

16. Show that Equ.(6.64) can be written in the form

$$\mu_f(T,\rho_n) = \mu_f(T,\rho_{n0}) - M_0 RT\,\upsilon_f(\rho_n - \rho_{n0})$$

where the index f refers to the solvent (fluid).

17. Two grams of CO_2 are dissolved in a liter of bottled water. Assuming that there only is carbon dioxide in the space above the water, how large is the pressure of the gas?

18. Calculate the equilibrium values of CO_2 in pure water for an atmosphere containing 280 ppmv and 380 ppmv carbon dioxide.

19. In pure water, some H_2O dissociates into H^+ and OH^-. Use the values of standard chemical potentials to calculate the concentration of H^+ in pure water in equilibrium (Table 6.10). What is the pH value of such water? (The pH value is defined as the negative decadic logarithm of the proton concentration.)

20. The partial specific volume (volume per mass) of nitrogen dissolved in sea water is 1.43 cm^3/g; it is 0.97 cm^3/g for oxygen. (a) Determine the pressure coefficients of the chemical potential for the gases. (b) With the density of sea water varying between 1.025 and 1.035 g/cm^3 (depending on its salinity), show that the solubility of nitrogen should decrease with increasing depth; the solubility of oxygen, on the other hand, might show an increase or a decrease with depth, depending on the density of sea water. (c) Calculate the expected percent change of solubility for the two gases when the depth changes by 1000 m. [Hint: You will have to consider both chemical and gravitational processes affecting the dissolved gas.]

21. Roughly 30 g of salt (NaCl) is dissolved in 1 liter of sea water. (a) Calculate the osmotic pressure of the salt with respect to the pure solvent (water) at a temperature of 300 K. (b) How high would the solution rise in an ideal cell with a semipermeable membrane separating it from the solvent?

22. Imagine a power plant at the mouth of a river flowing into the ocean, which uses the osmotic pressure difference between sea water and fresh water. If the river is carrying 1000

m^3/s of fresh water, how large could the power of an ideal plant be?

23. What is the change of entropy when dissolving 1 mole of table salt? How much entropy is produced in dissolving 1 mole of table salt? Is the process exothermic or endothermic?
24. At what temperature does sea water with a concentration of 35 parts per thousand freeze?
25. Is table salt more soluble at 45°C than at 25°C?
26. Solubility of O_2 in water is about 3.25 $cm^3/100cm^3$ at 25°C. (a) Determine the difference of the chemical potentials of O_2 as a gas and in aqueous solution. (b) At 0°C, the solubility is about 5 $cm^3/100cm^3$. Determine the temperature coefficient of the chemical potential of aqueous oxygen.
27. Predict the effect of a change of the pressure of the mixture of nitrogen, hydrogen, and ammonia from P_0 to P on the equilibrium composition. The ammonia synthesis proceeds according to

$$0 = 2NH_3 - 3H_2 + N_2$$

28. Determine the change of pressure accompanying a change of the melting point of ice. (a) Calculate the temperature and the pressure coefficients of the chemical potential of water and ice for 0°C, and then use Clapeyron's equation. The temperature coefficients of enthalpy of water and of ice are 4200 J/(K·kg) and 2100 J/(K·kg), respectively. (b) Use the fact that the energy needed to melt ice is 334 kJ/kg.
29. Mercury spilled in a room evaporates a little. A concentration of 0.1 mg/m^3 Hg in air is permissible during a work week. (a) At 25°C and 1.013 bar, Hg has a chemical potential of 31840 J/mole (see Table 6.11). The potential of liquid Hg is 0 J/mole. Does liquid Hg further evaporate in a pure Hg atmosphere, or rather, does mercury vapor condense (at 25°C and 1.013 bar)? Why? (b) Determine the equilibrium pressure (vapor pressure) of mercury vapor at 25°C. Treat the vapor as an ideal gas. (c) What is the equilibrium concentration in mg/m^3? The molar mass of Hg is 200 g/mole. How long would we be allowed to work in this room during a week? (d) How much higher or lower is the concentration of mercury vapor at 35°C?

Table 6.11: Mercury

	μ / kG	α / G/K
l	0	– 76
g	31.84	– 175

30. Give reasons to show that the diffusion of a substance through matter is completely dissipative. Assuming that this is correct, derive the entropy production rate for diffusion.
31. Assume that a muscle cell has concentrations of sodium ions (Na^+) of 20 mM and 145 mM on the inside and the outside, respectively; the solute is assumed to be the same inside and outside. (a) In what direction would sodium migrate if it were not charged? (b) What is the Nernst potential for this ion? (c) Are these ions in chemical equilibrium? In electrical equilibrium? In electrochemical equilibrium? (d) For the cell described, the actual electric potential difference across the cell membrane is – 90 mV during the so-called resting phase (the potential is lower inside). What is the net electrochemical driving force for Na^+? Where is the electrochemical potential lower? (e) For the same cell, the actual electric potential difference changes from – 90 mV to about + 20 mV during a so-called action potential event. At the peak of this event, what direction would Na^+ flow in?
32. Consider a system consisting of two cells filled with water having volumes of V_1 and V_2 (see Fig. P.32). There are two quantities n_1 and n_2 of a substance dissolved in the water. In cell 1, the substance is destroyed at a rate Π_{n1}; it is produced at a rate Π_{n2} in cell 2. The cells are separated by a membrane that is permeable to the substance. Assume the flow to be proportional to the difference of concentrations of the substance in the cells:

$$I_{n12} = r(c_1 - c_2)$$

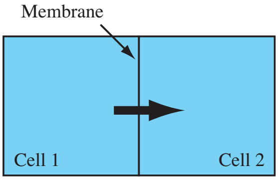

Figure P.32

The reaction in cell 1 is of the first order having a rate constant k_1, whereas the reaction in cell 2 is of order 0 (not dependent on concentration). The rate constant for the reaction in cell 2 is k_2. We are interested in the balance of the substance under consideration. (a) What are the units of the parameters r, k_1 and k_2? (b) Formulate the differential equations for n_1

and n_2. (c) Calculate the nontrivial equilibria of the systems, i.e., those for $n_1, n_2 \neq 0$, assuming that V_1, V_2, k_1, k_2, r are all greater than zero. Express the equilibria for n_1 and n_2 in a form that only contains system parameters.

33. Consider the radioactive decay of silver in Fig. 6.11. Include both isotopes in a model and formulate the differential equations for their amounts. Try to fit data by varying the initial quantities of the isotopes and the decay factors.

34. Nitrosyl bromide (NOBr) is a gas widely used in the chemical industry. Normally, it is produced by the reaction

$$2NO + Br_2 \rightarrow 2NOBr$$

Assume the reaction to run entirely in the indicated direction. (a) Formulate the equation for the rate of change of concentration of NOBr. (b) What is the rate of production of Nitrosyl bromide at $t = 0$ if you assume that there are 0.1 mole/L NO and Br_2 each, and that the rate constant of the reaction i s $1.2 \cdot 10^4$ $L^2/(mole^2 \cdot s)$? (This value of the rate constant is reached at about 250°C). (c) Sketch as carefully as possible the time evolution of the concentrations of all three substances. For initial conditions, assume that we have 0.1 mole/L NO and Br_2 each and no NOBr.

35. Consider a chemical reactor with a reaction $A + 2B \rightarrow C$. The volume of the reactor is equal to 5 liters. All reactants and products are assumed to be distributed homogeneously during the reaction. Initially, there are 2 moles of A, 1 mole of B, and no C in the reactor. The reaction rate is proportional to the concentration of A and to the square of the concentration of B. Assume the reaction to run completely in the indicated direction. (a) Assume that substances are not exchanged with the environment. Sketch the amounts of all substances as functions of time. Indicate important features of the behavior, including initial and final amounts of substance. (b) Assume now that the reactor is operated in steady-state which means that substances A and B have to be supplied and C has to be continually removed. Formulate the differential equations for the amounts of substances of all three chemicals. The right hand sides of the equations are supposed to contain only the concentrations, the volume of the reactor, the rate constant and the (constant) flows I_{nA}, I_{nB}, and I_{nC} of A, B, and C. (c) The reactions have to be kept in a steady-state (see Problem b) having the following properties: (1) I_{nC} is set to a value so that all of the produced C can be removed instantaneously. Let $I_{nC} = 1.0$ mole/h. (2) The concentration of A is constant at 4.0 mole/liter. What are the values of I_{nA} and I_{nB} that keep the system in this state? What will the amounts of substance n_A and n_B be in steady-state? Assume a rate constant of $k = 0.10$ $L^2/(mole^2 \cdot h)$.

CHAPTER 7

THE TRANSPORT OF HEAT

In this chapter, we shall take a closer look at the transport of entropy. Simple aspects will be introduced that go beyond what we already studied in Chapter 4 (Section 4.6). This extends the treatment of thermal processes into the realm of phenomena which are missing from the theory of the thermodynamics of ideal fluids (Chapter 5). Many texts on thermodynamics and on heat transfer sharply distinguish between the two subjects, which only emphasizes that a unified presentation of all thermal phenomena is called for. While we will not achieve the stated goal in this chapter, the ground will be prepared for a theory of continuum thermodynamics of which we will get a first glimpse in Part III.

The first section of this chapter provides a qualitative description of the three types of entropy transport: *conduction*, *convection*, and *radiation*. It introduces the formulation of the law of balance of entropy for a uniform body. Then, simple applications of all three forms of heat transfer will be discussed, giving an overview of some practical problems. Flow systems, i.e., open systems where fluids transport dissolved substances, entropy and momentum will be introduced in Chapter 8. There we extend the notion of chemical potential to fluids in flow systems.

Entropy production in heat transfer will be considered as we go along, preparing the ground for the concept of minimization of irreversibility in thermal design which will be applied in Chapter 9.

7.1 TRANSPORT PROCESSES AND THE BALANCE OF ENTROPY

In this section, I will describe qualitatively the basic phenomena underlying the transport of heat. Simple observations tell us that entropy can flow in three different ways: *conduction*, *convection*, and *radiation*. Consideration of these types of transport will lead to the formulation of the law of balance of entropy in a more general form than previously encountered, and will yield a better understanding of the role of hotness in thermal processes. In the end, the equation of balance of entropy will contain terms describing the different modes of transport.

These types of transfer processes are found not only in thermal physics, but in other fields of the natural sciences as well. Momentum transports have been classified in the same manner in Chapter 3. For this reason alone, it is important to have a clear understanding of the nature of entropy transfer.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_8,

7.1.1 Conductive Transport of Entropy

Heat one end of a metal rod over a flame; in a very short time the other end will feel hot as well. If you throw a hot stone in cold water, it will cool down while the water gets warmer. In a heat exchanger, a hot fluid flows through pipes, heating a cooler fluid which flows around the pipes. In all of these examples, entropy is removed from some bodies and added to others. Why else should some objects become colder while others heat up? The possibility of changing the temperature by compression, i.e., adiabatic processes, does not occur in these examples. Therefore we say that entropy has been transferred. Obviously, entropy flows from hotter to colder bodies.

How is entropy transported in these examples, and what are possible conditions for this process to occur? First, we observe that material transport cannot be involved. A piece of metal heated at one end retains its integrity. A hot stone does not dissolve in water, thereby spreading the entropy it contains. In the case of the heat exchanger, it is true that the fluids move; however, entropy must be transferred through the walls of the pipes. Heat therefore flows *through* bodies *without the help of a body transporting it*, and it flows from one body to another if the two are brought in *direct contact*. These are examples of heat conduction (*conduction* or *diffusion of entropy*).

An example that we studied in Chapter 4 tells us something about the role of temperature in the conductive transport of entropy. Two bodies having different temperatures are brought in thermal contact, and their hotnesses are monitored. It is found that the temperatures of the bodies change until they have become equal. As long as they are changing, entropy must be flowing: one of the bodies is cooled, the other is heated. In the end, however, the exchange stops. We conclude that entropy flows conductively as long as there is a difference of temperatures between the bodies exchanging heat, and that by itself, entropy flows only from hotter to colder objects.

Driving forces. This type of behavior is well known from a number of different physical phenomena. Connect two containers having different cross sections that are filled with water up to different levels; let the water flow between them. As a different example, connect two electrically charged spheres with a wire and monitor the electrical potential of each of the spheres. We know what will happen in both cases: the water levels in the containers will reach the same height, and the electric potentials of the two spheres will be the same after the process ends (Chapter 1). In each case, something flows as long as there is a difference of potentials, i.e., a *driving force*. In analogy to these well-known phenomena, we shall interpret the conductive transport of entropy as follows:

> *In conductive transport, entropy flows by itself through bodies from points of higher to points of lower temperature. In other words, entropy flows as long as there is a difference of temperatures, i.e., a thermal driving force.*

The balance of entropy. Conductive transport of heat is a prime example of an irreversible process (Section 4.6.3). A body conducting entropy produces more entropy at the same time. This must be so because in a steady-state process, the same amount of energy which enters the body at high temperature leaves it at a lower thermal level. Therefore, the current of entropy leaving the body must be larger than the one entering. Clearly then, the equation of balance of entropy must include the production term for entropy in addition to the term describing conductive transfer of heat into and out of the body:

$$\dot{S} = I_{S,cond} + \Pi_S \tag{7.1}$$

Here, $I_{S,cond}$ is the net current of entropy transported conductively with respect to the body in question. We call it the *conductive flux of entropy*.

Flow across surfaces. The conductive current is our way of describing a phenomenon in which we picture entropy to flow *across the surfaces of bodies*. If we are interested in the flow through a body we simply introduce imaginary surfaces inside. Again entropy flows across a surface where one part of a body touches another (Fig. 7.1). In this sense, conduction is a surface phenomenon, and it is rendered formal by a physical quantity, namely a flux I_S whose distribution over a surface is of prime interest (Chapters 11 and 13). We stress this point since a body can pick up or lose entropy in other ways (i.e., by radiation and sources of heat).

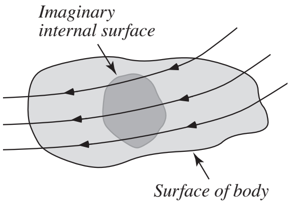

Figure 7.1: Conductive currents of entropy flow across surfaces. Such surfaces may be real surfaces of bodies or imaginary surfaces, such as those which we introduce to separate different parts of bodies. The flow lines in this figure do not reflect the fact that entropy is produced in conduction.

7.1.2 Transport of Entropy with Fluids: Convection

Northern Europe would be a pretty cold place to live were it not for the Gulf Stream, which transports huge amounts of heat from the Gulf of Mexico to the west coast of Europe. Our weather would be pretty dull were it not for the currents of hot or cold air in our atmosphere. These are just two important examples of a different mode of heat transfer. It is quite clear that in these cases entropy is transferred with the help of a material medium, like air or water. You can find examples all around you. Heated air rises from a radiator in a room; hot water which is pumped through the pipes of a central heating system delivers entropy to the radiators; water begins to boil at roughly 100°C, transporting entropy via a material current of steam. If entropy is carried by a material which is flowing we speak of *convective entropy transport*.

These examples demonstrate that convection is a very important phenomenon in our daily lives. We shall deal with some simple aspects of convection in Section 7.3. (More details will be provided in Chapters 8 and 14.) We are interested in a particular question at this point, the problem of the *driving force* of this type of heat transport.

The driving force. A difference of temperatures drives the conduction of entropy. You can easily see that this cannot be the driving force in the case of convection. The reason why hot water flows through pipes to your shower definitely cannot be found in a difference of temperatures: a pump drives the flow of water. The fact that the water is hot is immaterial to this transport phenomenon. We have to conclude that the cause of convective heat flow has to be sought in the driving force which lets the material substance (water, air, etc.) move: we know that this is a *pressure difference* set up by a pump or through some other device or process:

> *Entropy can be transported via a flowing substance. In this case, the flow of entropy is accidental. The driving force of the process is the difference of pressure which lets the material substance flow.*

There are some important examples of convection which might make us believe that a temperature difference must be the driving force of the process. Think of air rising above a hot radiator in a room. Also, the water circulating in a central heating system does so apparently because it is heated at one end (in the boiler). Indeed, the water does not flow if the heating is stopped.

Still, the immediate driving force for the flow of water (which is responsible for the transport of entropy in the system) is not a difference of temperatures but a *pressure difference caused by the heating*. The hot water in the boiler is slightly less dense than the surrounding liquid; therefore, it begins to rise as a consequence of buoyancy, which is a consequence of a pressure difference. The heating is responsible for the flow only in an indirect way. Another example is presented by our atmosphere: air can easily flow into a region where the temperature is higher. We call this phenomenon *free* or *natural convection* to distinguish it from convection induced by a pump, which is called *forced convection*.

The balance of entropy. Since convection and conduction are obviously different types of entropy transport, we should distinguish between them. For this reason, we also introduce *convective currents* in the equation of continuity of entropy:

$$\dot{S} = I_{S,cond} + I_{S,conv} + \Pi_S \tag{7.2}$$

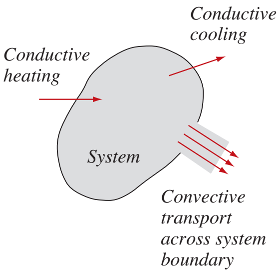

Figure 7.2: Entropy may flow across the boundary of a body either by conduction or by convection. In the former case, matter does not cross the surface and entropy flows through matter. In convection, a substance flows across the surface whereby entropy it contains is transported into or out of the system as well.

This equation tells us that the entropy content of a body can change as a consequence of two types of flow and the production of entropy (Fig. 7.2). Again, we are confronted with a surface phenomenon. Substance flows into and out of regions of space across surfaces, real or imagined. Just as in the case of conduction, we introduce fluxes to describe mathematically what is going on.

There is an important point to note. The transport of substance leads to changes of this quantity in regions of space influenced by the flow. Therefore, we have to be extremely careful to state what we are talking about, i.e., to identify the system (or element) for which we are performing a balance of entropy. So far, we have always used an identifiable material body as the physical system under consideration (Chapters 4 and 5). Such a body is assumed to retain its material integrity; i.e., it is not allowed to exchange matter with its surroundings. We shall continue to use the term *body* in this sense—an aggregate of matter which can always be identified and separated from the rest of the world. For a body such as a stone this identification is quite simple and clear. It is still simple in the case of air enclosed by rigid walls. In situations where matter flows, however, this becomes more difficult. Still, we may think of an identifiable amount of water moving with the flow of a river. This body of water is thought to be separated from the rest of the water by an imaginary surface which moves and deforms with the body (Fig. 7.3). If we have a body in mind, the balancing of quantities such as entropy always refers to this piece of matter. The time derivative of the entropy function (or of other functions) in Equ.(7.1) is taken for *the entropy of the body*. For this reason it is sometimes called a *material derivative*.

Control volumes. It is often more convenient to do the accounting with respect to a region of space rather than an identifiable body (Fig. 7.3). This is particularly true in cases where matter flows. Imagine a region of space surrounded by an imaginary surface. We often speak of a *control volume* and a *control surface* to distinguish it from bodies. A control surface may easily be penetrated by flows of matter, which leads to changes of the amount of substance in the control volume. This is the case if we consider convective currents, as we have done above. The time derivative of the entropy in Equ.(7.2) is not taken with respect to a body, but with respect to some control volume (which may be stationary or moving). The derivative, therefore, is of *the entropy of the control volume*. We will learn later how to distinguish mathematically between this derivative and a material one. By the way, systems which may exchange matter are called *open*, while those which do not are called *closed*. Bodies are closed systems by definition.

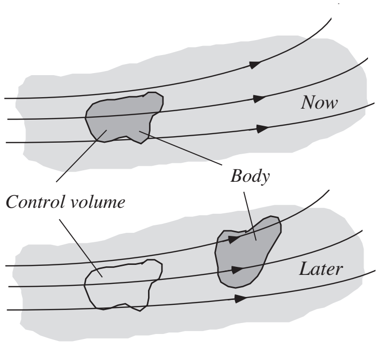

Figure 7.3: A body and a control volume in a general situation involving the flow of substance. A body moves and deforms with the flow. A control volume is any region of space, itself moving or stationary. In general, a control volume is penetrated by convective currents. In this example, the body and control volume occupy the same region of space initially.

7.1.3 Transport of Entropy with Radiation

It is obvious in some cases that entropy is transported neither by conduction nor by convection. Take the heat of the Sun, which travels to us through empty space, covering a distance of 150 million kilometers. It is clear that the Sun must radiate heat since it produces vast amounts of entropy all the time without changing noticeably. The transport cannot be via conduction. Also, there is no material substance which can act as a carrier of entropy in a convective process.

Heat which is emitted by warm bodies can even be photographed. You can see objects on infrared films. They look unfamiliar, but the process clearly is similar to photography with normal light. This suggests that there is a medium which transports heat in these cases after all. This medium would be similar to light. Indeed, this is the accepted picture: electromagnetic radiation (X-rays, ultraviolet, visible, infrared, or radio frequency) carries heat. Hot bodies emit electromagnetic radiation which then transports heat.

One group of phenomena is so pervasive that it makes us think that some bodies must radiate heat (entropy). (On closer inspection, however, you may realize that these phenomena are not the kind of proof we are looking for.) You can sit behind a glass window and feel the heat of the Sun's radiation. You can observe the same phenomenon when you sit by a fire; while all the heated air might go up the chimney, you still get hot sitting there. Meals can be kept hot by lamps, and again conduction or convection are not responsible for the flow of heat. The problem with these cases is that the heat felt by the bodies absorbing radiation may be produced inside them. Indeed, in the case of solar radiation, almost all the entropy which appears in a body absorbing the Sun's rays is created in the body (see Chapter 16 on solar radiation).

Transport through the radiation field. We call this type of transport the *radiation of heat*. It is interpreted as the flow of entropy (and other quantities) through a physical system different from normal bodies, namely the *electromagnetic field*. The transport through the field takes place with radiation which can store and transport such quantities as entropy, momentum, and energy, just like ordinary materials. W can write down an equation of balance of entropy for the electromagnetic field in an otherwise empty control volume (Fig. 7.4):

$$\dot{S}_{field} = I_{S,rad} \tag{7.3}$$

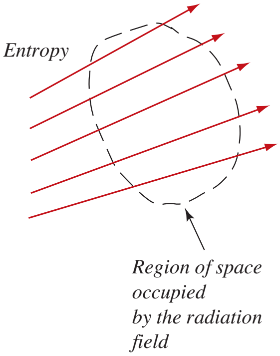

Figure 7.4: Imagine an empty region of space between the Sun and the Earth. Entropy is transported with radiation through this control volume. There is no difference between temperatures across the region.

The flow of entropy through the field is a surface phenomenon with currents flowing across imaginary surfaces drawn around regions of space. The amount of entropy in a region of space occupied by a radiation field changes as a consequence of the transport of entropy together with radiation into and out of the region (Fig. 7.4). The flow of heat through empty space is not dissipative. As a simple example, consider two imaginary spheres drawn concentrically around the Sun, the first near its surface, the second much further out. Later in this chapter and in Chapter 12 we will learn how to compute the flux of entropy through surfaces cutting through the radiation field. We will find that the same amount of entropy flows through both spheres in the same time span. Therefore the rate of production of entropy for a region of space which contains only the radiation field is zero.

It is interesting to ask whether we need a difference of temperatures for entropy to flow radiatively through the electromagnetic field. In fact, this is not the case. We associate the same temperature with the radiation which has just left the Sun and with the radiation that arrives at the Earth. In this sense, radiative transfer of entropy has much in common with convective transport. The driving force for the transport, if one is needed at all, is not the thermal driving force responsible for conduction. This is of profound importance for the determination of the relationship between fluxes of entropy and of energy (see Section 7.4). Put simply, there is a great difference between entropy flowing by itself in conductive transport, and entropy being carried by something else, be it water or radiation.

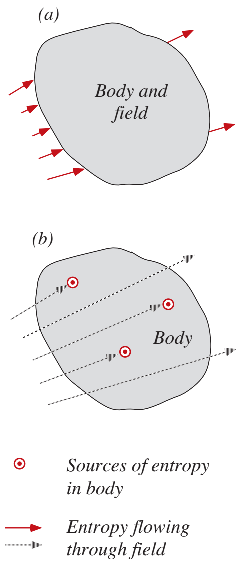

Figure 7.5: The same region of space as in Fig. 7.4 is now filled with matter such as air. Field and body can occupy the same space at the same time. For this reason their interaction takes place at every point inside the system. If we consider the material body only, we have to introduce sources of entropy where the body absorbs radiation from the field, and sinks where it emits entropy to the field.

7.1.4 Interaction of Bodies and Fields

Often, we are not interested in the transport of entropy through the radiation field but rather in the interaction of fields and bodies. The example of the Sun emitting radiation and of the radiation penetrating the Earth's atmosphere can tell us much about this interaction. The radiation which is not reflected back into space enters the atmosphere, where part of it is absorbed along the way to the surface of the Earth. We know from experience that only part of the radiation is absorbed; the rest reaches the surface. At the same time, the air must emit entropy since it cannot continually absorb radiation without getting hotter and hotter. Absorption and emission take place in every part of the atmosphere. This means that the radiation field pervades the air; it does not stop where the layer of air surrounding our planet begins. In other words, *the radiation field and the atmosphere occupy the same region of space* at the same time (Fig. 7.5).

The balance of entropy for body and field. To motivate the law of balance of entropy in the case of radiative transfer, we shall proceed in two steps. First, consider the combined system of matter and field occupying some region of space (Fig. 7.5a). In the case of solar radiation interacting with the Earth's atmosphere, this system absorbs some of the radiation flowing through the field. As far as the region of space is concerned, we have only radiative fluxes of entropy with respect to its surface. (Neglect for the moment that entropy may be conducted through air, and that air may flow through the system.) The entropy of the system may change only due to such radiative currents and the production of entropy in case of dissipation:

$$\dot{S} = I_{S,rad} + \Pi_S \tag{7.4}$$

Indeed, as we shall learn in Section 7.4, the absorption and emission of entropy are irreversible processes. For this reason, we may not neglect the production term.

However, we are often interested only in the balance of entropy with respect to the body alone (Fig. 7.5b). In this case, we have to consider the interaction of matter with the part of the field which occupies the same space. The interaction between the two, if it takes place at all, takes the form of absorption of radiation from the field by the body, or emission from the body to the field. Absorption and emission take place at every point in space occupied by the two systems. The properties of the body and of the field determine the amount of entropy which is absorbed or emitted.

Sources due to absorption and emission. Absorption and emission of radiation are not surface phenomena, but rather *volumetric processes*. In the absorption of radiation by the Earth's atmosphere there is no flow of entropy through this material body. Entropy enters the material system via the field, which means that there are *no currents through matter* associated with this type of transport. It simply appears at every point depending upon the degree of interaction. If we write an equation of balance of entropy for the material body only, we have to represent the interaction using a *source term* instead of currents:

$$\dot{S}_{body} = \Sigma_{S,body} \tag{7.5}$$

Here, $\Sigma_{S,body}$ is the *entropy supply* or *source strength of entropy* which is the net time rate at which entropy enters or leaves the body as a result of the interaction. The equation of balance of entropy of the field, on the other hand, must take the form

$$\dot{S}_{field} = I_{S,rad} + \Sigma_{S,field} \tag{7.6}$$

If we now combine the last two equations, we obtain:

$$\dot{S}_{body} + \dot{S}_{field} = I_{S,rad} + \Sigma_{S,body} + \Sigma_{S,field} \tag{7.7}$$

Comparison of this expression with Equ.(7.4) tells us that entropy must have been produced as a result of emission (or absorption) of radiation by the field and absorption (or emission) by the body. In other words, more entropy is absorbed by the body than is emitted by the field. The relation between the two source rates and the rate of production of entropy must be given by

$$\Sigma_{S,body} + \Sigma_{S,field} = \Pi_S \tag{7.8}$$

with the entropy being produced as a result of the transfer between the field and the body (Fig. 7.6). Note that we have to distinguish between sources of entropy due to entropy production and transfer between fields and bodies. Both effects are volumetric, in contrast to flows (conductive and convective).

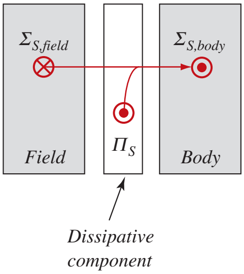

Figure 7.6: If we model the result of the transfer of radiation from the field to the body as uniform heating of the body, we have the problem of deciding where to include the source of irreversibility. The solution presented in the equations corresponds to introducing a dissipative component between the field and the body.

The general law of balance of entropy. If we now include the source term with the conductive and convective fluxes and the production of entropy in Equ.(7.2), we finally obtain the most general case of the equation of balance of entropy for a body:

$$\dot{S} = I_{S,cond} + I_{S,conv} + \Sigma_S + \Pi_S \tag{7.9}$$

This equation includes all the processes we are going to discuss. It expresses the fact that the entropy of a body may change as a result of three distinct types of transport: conductive, convective, and radiative, and the effects of irreversibility.

7.1.5 The Balance of Energy

One of the most important practical problems in the theory of heat transport is the determination of the fluxes and source terms of entropy in the equation of balance (see Equ.(7.9).) We have to find the constitutive laws which let us calculate these quantities in concrete situations. At this point, the energy principle will come to our aid. All three types of entropy transport are accompanied by the flow of energy. For this reason we should consider the law of balance of energy alongside that of entropy. Since energy is a conserved quantity, the amount stored in a body can change only by way of transfer to or from another system. The type of transfer of energy depends on the type of entropy flow. In the cases of conduction and convection, energy flows with entropy across system boundaries. This means that in these cases it is accounted for in terms of conductive or convective currents. If entropy is transferred radiatively, however, the interaction of bodies and fields leads to sinks or sources of energy in the body (or in the field). As a result of entropy transfer, energy either flows across system boundaries, or it pours into bodies via a radiation field. Therefore we distinguish between two types of currents and a source term of energy for material systems:

$$\dot{E}_{body} = I_{E,cond} + I_{E,conv} + \Sigma_{E,body} \tag{7.10}$$

For the radiation field alone, the equation of balance of energy must take the form

$$\dot{E}_{field} = I_{E,rad} + \Sigma_{E,field} \tag{7.11}$$

The last term on the right-hand side of Equ.(7.10) is the *source rate* or the *supply of energy*. Actually, in Equ.(7.10), we have neglected the transport of energy due to other processes such as mechanical ones. In the case of convective currents we cannot always do this. However, for the purpose of this chapter we shall regard such contributions as negligible compared to the other terms.

As we shall see, the relationship between entropy and energy in thermal transport phenomena will help us greatly in resolving the constitutive problem. To be specific, we are interested in a number of relationships, namely those between:

- Fluxes of entropy and energy in conduction.
- Fluxes of entropy and energy in convection.
- Fluxes of entropy and energy through the radiation field.
- Sources of entropy and energy.
- Energy and the production of entropy.

The following sections will in turn deal with different modes of transport. The one type of relationship between entropy and energy in thermal processes that we have considered so far (remember Equ.(4.21) in Chapter 4) is not of a general nature for transport. Rather, convection and radiation must lead to different expressions relating fluxes of entropy and energy.

In the following sections we shall introduce some simple aspects of all three modes of heat transfer to gain some idea of the breadth of applications. We will encounter a simple version of heat conduction, a discussion of the radiation of heat from surfaces, and an introduction to heat transfer from solid bodies to fluids (or vice versa). In later chapters, conduction, convection, and radiation will be presented in more depth.

QUESTIONS

1. What is the driving force for a conductive transport of entropy? What is it for a convective flow of entropy?
2. When (hot) water flows out of a tank, there is a convective entropy current leaving the system. Does this mean that the water in the tank gets colder?
3. In the case of flows and sources of entropy, entropy is transported from one system to another. So, what is the (geometric or spatial) difference between a current of entropy and an entropy source rate?
4. Both source rates of entropy and entropy production rates are volumetric quantities. What is their difference?
5. If a body of air in the atmosphere absorbs some solar radiation, are the energy source rates of the radiation field and of the air equal? Are the entropy source rates equal?

EXAMPLE 7.1. Conductive and convective fluxes of entropy.

Consider hot water flowing through a metal pipe as in the figure below. (a) Consider the interior of a part of the pipe as the system, and assume this control volume not to move or deform. Account for all fluxes of entropy penetrating the surface of this control volume. (b) Consider the water in the control volume at a particular instant to be the system. Follow this body of water in its motion and repeat the problem (a).

SOLUTION: a) We are dealing with a stationary control volume (*CV*) through which water and entropy are flowing. (See the upper part of Fig. Ex.1; water is flowing from left to right.) We have to find the currents flowing through the control surface and determine the fluxes associated with them.

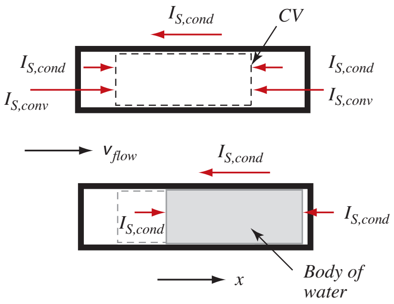

Figure Ex.1

First of all, entropy must be flowing radially outward through the pipe if the surroundings are cooler than the water. This means that we have a *conductive* current of entropy penetrating the cylindrical surface. Since the flow is outward, its flux will have a negative sign (symbolized by an arrow in the negative *x*-direction).

Second, because of the loss of heat through the walls of the pipe, the water entering the control volume will be warmer than the water leaving. We have a thermal driving force in the direction parallel to the axis of the pipe. At the control surface, there must be conductive currents of entropy through the water in its direction of flow. Therefore, we have a positive flux associated with the conductive current at the entrance to the control volume (left), and a negative flux due to the current leaving the system.

Finally, two convective fluxes are associated with the flow of water into and out of the control volume. Entropy stored in the water is carried across the surface of the system. Again the flux is positive at the inlet, and negative at the outlet. The flux at the entrance is larger in magnitude than the one at the outlet.

(b) If we follow a certain body of water in its motion, the system wall moves with it (lower part of Fig. Ex.1). Water does not flow across the surface of the body, which is represented by the shaded area. This means that there are no convective currents of entropy to be considered. The conductive currents still exist, and they are the same as the ones identified in (a).

7.2 CURRENTS OF ENTROPY IN CONDUCTION

We have considered the generic expressions for laws of balance of entropy and energy in the previous section. Now we shall turn our attention to the constitutive theories that will allow us to quantify entropy transfers. Let me begin with conduction.

7.2.1 Fourier's Law for Entropy

What factors does the current of entropy in conductive transport depend upon? If the temperature of a body changes from place to place, there must be *temperature gradients*. This is one factor upon that we expect the rate of flow of heat, the entropy current, to depend. The material through which the entropy flows must also play a role in the determination of the current. The influence of the material will be described by its *conductivity*. If the current of entropy depends upon the temperature gradient and the conductivity in the simplest possible way, we say that it obeys *Fourier's law*.

Fourier's law for a slab of matter. We can motivate the form of Fourier's law in a simple manner. The idea is borrowed from electricity, where we also have encountered phenomena having to do with conduction, namely the conduction of charge (Chapters 1). Consider the conduction of entropy through a slab of material as shown in Fig. 7.7. Assume that entropy flows only in one direction, and that the distribution of the current of entropy does not vary in a plane perpendicular to the flow. In other words we will consider only the simplest possible case of a flow field.

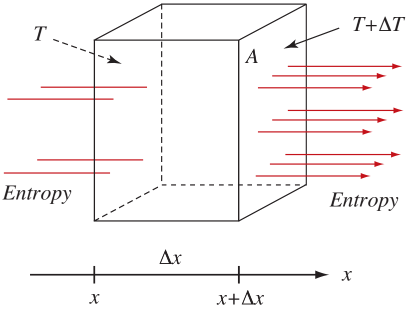

Figure 7.7: Entropy flows in one direction only through a slab of matter. We assume that the distribution of the current does not vary in planes perpendicular to the *x*-direction. There is a difference of temperatures between front and back faces which serves as the driving force of the flow of entropy.

The basic question is this: how does the current density of entropy depend upon the circumstances? From what we already know, the current of entropy through a body should depend upon the temperature difference across the body (in the direction of the flow of entropy) and a conductance that depends upon the geometry and the conductive properties of the body. The conductance is what we should be concerned with here. Clearly, for given temperature difference, the current doubles if the cross section A of the conducting body doubles: we simply have two equal conducting bodies in parallel. Secondly, we expect the current to halve if the thickness of the slab is doubled. Therefore,

$$I_S(x) = -k_S \frac{A}{\Delta x} \Delta T \tag{7.12}$$

The negative sign tells us that entropy flows into the body at x (Fig. 7.7); remember that the temperature difference is negative. The factor k_S quantifies the conducting property of the material; it is called the *entropy conductivity* of the substance.

This is *Fourier's law* of conduction. Naturally, the entropy conductivity is expected to depend upon the material the body is made up of, and on temperature (Fig. 7.8). Some values of entropy conductivities are given in Table 7.1.

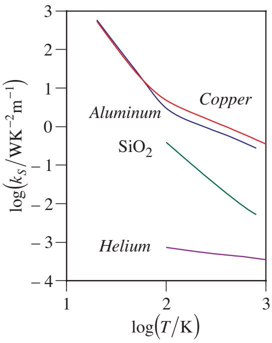

Figure 7.8: Some entropy conductivities k_S as functions of temperature. The values of the conductivities with respect to energy, i.e., those commonly listed in tables, are equal to k_S multiplied by the temperature of the material (Fig. 7.9).

Table 7.1: Conductivity of some materials

Substance	**Conditions**	**Conductivity (entropy)**	**Conductivity (energy)**
	300 K	k_S / W · K^{-2}m^{-1}	k_E / W · K^{-1}m^{-1}
Gases at atmospheric pressure			
Air	200 K	$9.05 \cdot 10^{-5}$	0.0181
	300 K	$8.73 \cdot 10^{-5}$	0.0262
	400 K	$8.41 \cdot 10^{-5}$	0.0337
Helium	200 K	$5.89 \cdot 10^{-4}$	0.1177
CO_2	250 K	$5.16 \cdot 10^{-5}$	0.0129
	300 K	$5.53 \cdot 10^{-5}$	0.0166
H_2O vapor	400 K	$6.52 \cdot 10^{-5}$	0.0261
	500 K	$6.76 \cdot 10^{-5}$	0.0339
	600 K	$7.03 \cdot 10^{-5}$	0.0422
Saturated liquids			
Mercury	293 K	$2.97 \cdot 10^{-2}$	8.69
Water	273 K	$2.02 \cdot 10^{-3}$	0.552
	293 K	$2.04 \cdot 10^{-3}$	0.597
	313 K	$2.01 \cdot 10^{-3}$	0.628
	333 K	$1.96 \cdot 10^{-3}$	0.651
	353 K	$1.89 \cdot 10^{-3}$	0.668
	373 K	$1.82 \cdot 10^{-3}$	0.680
Liquid metals			
Sodium	366 K	0.232	84.96

Table 7.1: Conductivity of some materials

Substance	Conditions 300 K	Conductivity (entropy) k_S / W · K^{-2}m^{-1}	Conductivity (energy) k_E / W · K^{-1}m^{-1}
Solids at 20°C			
Aluminum		0.80	240
Brick (building brick)		0.0024	0.7
Bronze (75% Cu, 25% Sn)		0.089	26
Clay		0.0043	1.3
Concrete (cinder)		0.0026	0.76
Copper	300 K	1.32	400
	500 K	0.772	386
	800 K	0.458	366
Fiber (insulating board)		$1.6 \cdot 10^{-4}$	0.048
Glass (window)		0.0027	0.8
Glass fiber		$1.3 \cdot 10^{-4}$	0.038
Granite		0.0058–0.014	1.7–4.0
Iron	300 K	0.27	80
	500 K	0.12	61
Lead	300 K	0.12	35
Limestone	100–300°C		1.3
Paper		$3.6 \cdot 10^{-5}$	0.011
Pyrex		0.0046	1.4
Rubber (vulcanized, hard)		$4.3 \cdot 10^{-5}$	0.013
Sand		$8.9 \cdot 10^{-5}$	0.027
Sandstone		0.0061	1.83
Steel	1.0% C	0.15	43
	20% Ni	0.065	19
Tissue	Fat layer	0.00066	0.20
	Muscle	0.0014	0.41
Tungsten		0.556	163
Wood	Oak	0.00057	0.166
	White pine	0.00038	0.112

The differential form of Fourier's law. To prepare the ground for treating the continuous case (Part III), let me transform the expression for a conductive current of entropy. Experience tells us that the conductive transport of heat violates our assumption of spatial uniformity: temperatures must change from point to point inside the materials conducting entropy. Therefore, Equ.(7.12) is not the best possible expression for a conductive current of entropy. Also, if you remember the treatment of heat transfer in Chapter 4, you will notice that Equ.(7.12) cannot hold for every point inside the slab through which heat is conducted. Conduction is dissipative, meaning that entropy is produced as it flows through the body. In other words, the entropy current increases in magnitude in the direction of flow and we have to specify where we want to apply Equ.(7.12).

All these difficulties disappear in a continuum description of the phenomenon (Chapters 11 and 13). At this point, all we should do is take a first look at Fourier's law in the continuous form. In a first step, we introduce a measure of the distribution of the current over the surface through which it flows, namely the current density j_S. In our case, it is related to the magnitude of the flux I_S as follows:

$$|I_S| = A\,|j_S| \tag{7.13}$$

The meaning of the density of a current of entropy will be explained in more detail in Chapters 11 and 13. The unit of the current density of entropy is W/(K·m^2).

Equ.(7.12) indicates how we can proceed. The term $\Delta T/\Delta x$ in Fourier's law is changed to the *temperature gradient dT/dx*. The conductivity keeps its meaning, so we arrive at

$$j_S = -k_S \frac{dT}{dx} \tag{7.14}$$

It is clear that the current of entropy must vanish if the temperature gradient is zero. In the simplest case, the current density will depend linearly upon the gradient. Also, entropy is not conducted if we deal with a perfect insulator whose conductivity is zero. For these reasons, Equ.(7.14) makes sense. It is perfectly analogous to what we have seen in the case of the conduction of momentum or electric charge (Chapter 3). Note that we have not yet solved the constitutive problem of the conductive transport of heat. While we now have a relation for the current of entropy appearing in the equation of balance, we still do not have an expression for the rate of generation of entropy.

7.2.2 The flow of entropy and energy in conduction

A current of energy is always associated with a current of entropy in conductive transport. According to Equ.(4.21), the former is equal to the latter multiplied by the temperature of the material at the point where the two flow together. This relation carries over to the continuous case:

$$j_{E,th} = T\,j_S \tag{7.15}$$

Just as there is a current density of entropy, there also must be a current density of energy. Equ.(7.15) holds for every point in a body through which entropy flows conductively. The validity of the generalization of $I_E = TI_S$ can be proved more rigorously (Chapter 12). For now, let us accept it as intuitively clear. If we introduce the definition of the *conductivity with respect to energy* (*thermal conductivity,* Fig. 7.9),

$$k_E = T\,k_S \tag{7.16}$$

Fourier's law can be expressed in terms of the thermal energy current:

$$j_{E,th} = -k_E \frac{dT}{dx} \tag{7.17}$$

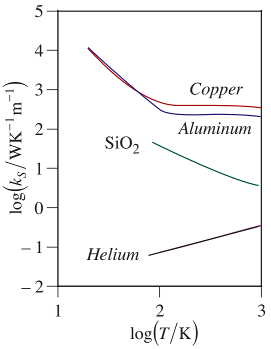

Figure 7.9: Some thermal conductivities k_E as functions of temperature. See Fig. 7.8 for the equivalent entropy conductances.

Since we consider pure conduction of heat, only the thermal energy current appears in a process. Therefore, the expression for the balance of energy will take a particularly simple form.

7.2.3 Entropy Production in Conduction

The conductance of a fluidlike quantity is a prime example of an entropy producing process. Here are two ways to determine the entropy production rate in conduction of entropy.

Dissipation. If entropy enters the hot end of a slab of material and exits at the cold end, as shown in Fig. 7.7, entropy is produced inside. This is so because the entropy falls from a high to a low level thereby releasing energy which is dissipated. From what we have studied in Chapter 4 (Section 4.6.3) we know that

$$\Pi_S = -\frac{1}{T_{\mathrm{L}}}\Delta T\, I_S = \frac{1}{T_{\mathrm{L}}}\Delta T\, k_S \frac{A}{\Delta x}\Delta T$$

or

$$\Pi_S = \frac{1}{T_{\mathrm{L}}} k_S A\,\Delta x\left(\frac{\Delta T}{\Delta x}\right)^2 \tag{7.18}$$

The volume *density of the production rate* is introduced in the continuous case. It is obtained by dividing the expression in Equ.(7.18) by the volume of the slab:

$$\pi_S = \frac{1}{T} k_S\left(\frac{dT}{dx}\right)^2 \tag{7.19}$$

The term $T\pi_S$ is the *density of the dissipation rate* inside the material as a consequence of conduction.

Simultaneous balances of entropy and energy. Here is a type of derivation which will prove very useful in many applications. The first approach just outlined requires us to have direct knowledge of the amount of energy dissipated, and the temperature at which dissipation takes place. If we do not have this (or are unsure about the values), there is an indirect method that uses the balance of energy to determine the missing constitutive relation, i.e., the production rate of entropy.

Consider a resistive element similar to the slab of matter in Fig. 7.7. The laws of balance of entropy and of energy for this body take the forms

$$\begin{aligned} 0 &= I_{S1} + I_{S2} + \Pi_S \\ 0 &= I_{E,th1} + I_{E,th2} \end{aligned}$$

Since we assume that the resistive element does not store entropy or energy, rates of change of entropy and energy must equal zero. Together with the relations between current of entropy and energy,

$$\begin{aligned} I_{E,th1} &= T_1 I_{S1} \\ I_{E,th2} &= T_2 I_{S2} \end{aligned}$$

we arrive at

$$\Pi_S = -\left(I_{S1} + I_{S2}\right) = -\left(\frac{1}{T_1} I_{E,th1} + \frac{1}{T_2} I_{E,th2}\right)$$
$$= -\left(\frac{1}{T_1} I_{E,th1} - \frac{1}{T_2} I_{E,th1}\right) = -\frac{T_2 - T_1}{T_2}\frac{1}{T_1} I_{E,th1} = -\frac{T_2 - T_1}{T_2} I_{S1}$$

which is equivalent to what we have derived before. Here we did not assume knowledge of the dissipation rate; the rate of dissipation is part of the combined laws regarding entropy and energy in a specific situation.

7.2.4 Calculation of Conductances or Resistances

In Section 4.6.1, the conductance (or its inverse, the resistance) for overall heat transfer through a series of transfer layers has been introduced. The definition carries over to a single (conductive) layer. Hence,

$$G_{S,cond} = k_S \frac{A}{\Delta x} \tag{7.20}$$

The resistance of such a layer is therefore equal to

$$R_{S,cond} = \frac{\Delta x}{k_S A} \tag{7.21}$$

The entropy transfer coefficient h_S (Equ.(4.45)) can be calculated from this, and all of this can be converted to energy related quantities (Equ.(4.47)). According to Section 4.6.4, conductances or resistances can be calculated for composite layers. It is customary to do this for the energy flow resistances or conductances (by assuming them to be independent of temperature). For a *series* of layers we get

$$R_{E,cond} = \sum R_{E,i} \tag{7.22}$$

and for *parallel* layers

$$G_{E,cond} = \sum G_{E,i} \tag{7.23}$$

Remember that these rules have to be taken with a grain of salt. Thermal properties such as conductances typically vary with temperature (Table 7.1 and Fig. 7.8). If we wish to do the calculations directly for the entropy conductances we have to take into account entropy production which, for series connections, leads to Equ.(4.55). If temperature differences are relatively small, and if property values are relatively uncertain, we can use Equ.(7.22) directly for the total entropy resistance as well.

7.2.5 A Dynamical Model of Conduction in a Copper Bar

To demonstrate the utility of the assumptions behind Fourier's law, let us work on a dynamical model of conduction in a long copper bar. An example of experimental data was presented in Chapter 4 (Section 4.1, Fig. 4.5) where a copper bar was stuck in ice water at one end and heated electrically at the other. First, before the electric heater was turned on, temperatures went down, those close to the end in ice water reacted first, then those farther away. With the heating on, temperatures went up, first those close to the heater, then those further down the line.

Even though we do not have the tools yet to treat the continuous case found in nature, we can still produce a useful model based on uniform bodies by dividing the copper bar into several elements. We view each element as a store for entropy having its temperature (which we associate with the center of the element; Fig. 7.10, top). The material between two center points is taken as the conductive piece (or resistive element) between two storage units.

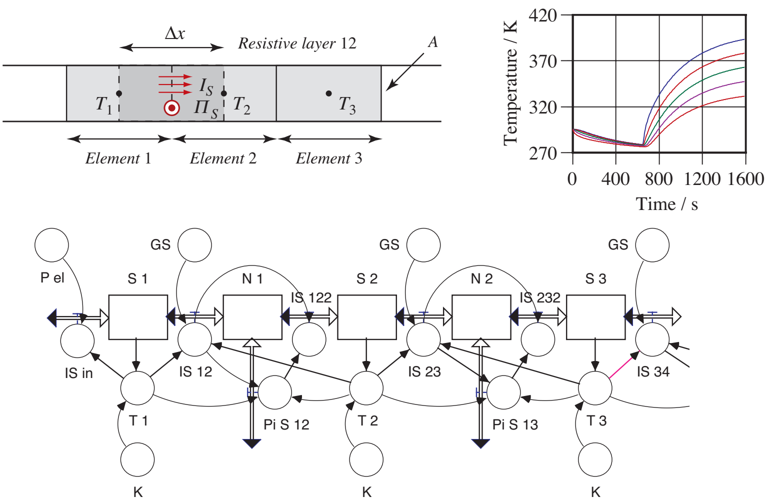

Figure 7.10: A long conducting bar is divided into elements (top left). An element is a storage unit for entropy. The material between (the centers of) two elements is modeled as a resistive element. Bottom: Section of a diagram of a dynamical model for this system. Note the entropy stores and the nodes (used to express the balance of entropy for the resistors). Top right: Simulation results for a particular case (compare to Fig. 4.5).

Length and cross section of an element define the geometry needed to calculate entropy capacitances (Chapter 4) of elements and conductances of resistors (Equ.(7.20)). The model can be simulated with proper initial and boundary conditions (see the graph in Fig. 7.10).

QUESTIONS

6. How large is the entropy current through a 10 m by 10 m sandstone wall which is 0.5 m thick if the temperature difference is 20°C?
7. Assume constant (temperature independent) entropy resistances of a couple of layers placed in series. Why can't we simply add them to get the total resistance?
8. Consider two conducting bars like the one in Fig. 7.10 made of two different materials. They are geometrically equivalent and have equal conductivities and specific entropy capacitances. The second material has a higher density. How would the behavior of the second material differ from that shown in Fig. 7.10?
9. Temperatures have been measured at 8 points along the copper bar in Fig. 7.10. Does this mean the dynamical model should be made of 8 elements?

EXAMPLE 7.2. Melting a block of ice insulated in glass fiber.

A cube of ice having a volume of 1.0 m^3 is in a box insulated by 10 cm thick glass fiber. It is left in an environment at 30°C. Estimate how long will it take for the cube to melt.

SOLUTION: Treat the layer of glass fiber as a flat blanket having a surface area of 6 m^2 (this is the surface area of the cube of ice). According to Table 7.1, the entropy conductance of glass fiber is 1.3 · 10–4 W/(K^2 · m). Therefore, the entropy current from the environment to the ice is

$$I_S = -k_S \frac{A}{\Delta x} \Delta T = -1.3 \cdot 10^{-4} \frac{6.0}{0.10} (0 - 30) \frac{\text{W}}{\text{K}} = 0.23 \frac{\text{W}}{\text{K}}$$

The 1.0 m^3 of ice corresponds to 910 kg. The specific latent entropy of ice is l_f = 22/0.018 J/(K · kg) (Chapter 5, Table 5.1). Therefore, the latent entropy of the block is 1.1 · 10^6 J/K. The time taken to supply this much entropy to the volume of ice is

$$\Delta t = \frac{S_e}{I_S} = \frac{1.1 \cdot 10^6}{0.23} \text{s} \approx 5 \cdot 10^6 \text{s}$$

This corresponds to close to 60 days. Naturally, the model assumes that the melt water stays at a temperature of 0°C and transmits entropy easily (i.e., it is assumed the melt water does not blanket the ice in addition to the sheets of glass fiber).

EXAMPLE 7.3. Heating of an integrated circuit.[1]

A silicon chip is attached to an isothermal surface called a *header*. The top of the chip is covered uniformly by a power device which dissipates energy at a rate of 50 W. Thirty thin gold wires connect the top with the header. Assume the entropy to be conducted down through the chip in one direction only. What will the steady-state temperature be at the top of the chip, if the header is kept at a temperature of 25°C?

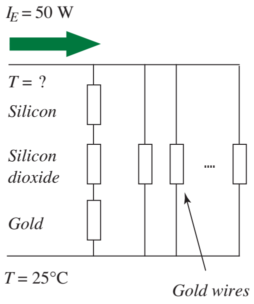

Figure Ex.3

The chip has a surface area of 0.51 cm by 0.51 cm. It is composed of three layers. The first is made out of silicon with a thickness of 0.051 cm. The chip carries a thin layer of gold at the bottom; its thickness is 0.010 cm. Between these two a thin layer of silicon dioxide forms, which has a thickness of 0.00013 cm. The thermal conductivities with respect to energy are 88 W/(K · m), 312 W/(K · m), and 0.157 W/(K · m), respectively. The gold wires are 0.130 cm long and have a diameter of 0.0254 cm.

SOLUTION: The device represents a thermal circuit with elements in parallel and in series (see figure). A constant thermal driving force is maintained over the circuit. We must figure out the total thermal resistance offered by the circuit to the flow of entropy and energy. The chip has a resistance of

$$\begin{aligned} R_{E,chip} &= \sum_{i=1}^{3} \frac{1}{k_{E,i}} \frac{\Delta x_i}{A} \\ &= \frac{1}{0.0051^2} \left(\frac{0.051 \cdot 10^{-2}}{88} + \frac{1.3 \cdot 10^{-6}}{0.157} + \frac{0.010 \cdot 10^{-2}}{312} \right) \frac{\text{K}}{\text{W}} = 0.554 \text{ K/W} \end{aligned}$$

This device is connected in parallel with thirty identical wires. Therefore, the total resistance is calculated to be

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[1] P. Ridgely (1987).

$$\frac{1}{R_{E,tot}} = \sum_{i=1}^{31} \frac{1}{R_{E,i}} = 30\frac{k_E A}{\Delta x} + \frac{1}{R_{E,chip}}$$

$$= 30\frac{312 \cdot \pi (1.27 \cdot 10^{-4})^2}{0.0013}\frac{\mathrm{W}}{\mathrm{K}} + \frac{1}{0.554}\frac{\mathrm{W}}{\mathrm{K}} = 2.17\frac{\mathrm{W}}{\mathrm{K}}$$

This corresponds to a resistance of 0.461 K/W. With the energy flux given, we can calculate the thermal driving force, i.e., the difference of temperatures between the top and the bottom of the chip:

$$\begin{aligned}\Delta T &= R_E I_{E,th} \\ &= 0.461\mathrm{K/W} \cdot 50\mathrm{W} = 23.0\mathrm{K}\end{aligned}$$

The temperature at the top of the chip is 48°C. Without the gold wires it would be 53°C.

EXAMPLE 7.4. A model of two uniform bodies in thermal contact

The faces of two identical cylinders, one heated to a high temperature T_{1i} and the other to a low temperature T_{2i}, are brought in direct thermal contact. (a) Calculate their temperatures as functions of time by treating them as spatially uniform bodies. (b) Compare the result to a finite element computation of the temperatures of their centers. (c) Calculate the entropy produced.

SOLUTION: (a) The model can be constructed along the lines of the model presented in Fig. 7.10. We have two bodies touching directly (see Fig. Ex.4.1). They are treated as spatially uniform stores of entropy. We can imagine the entropy to travel on average from the center of the warmer to the center of the colder body, so we use the matter between the two centers as the conductive transfer layer.

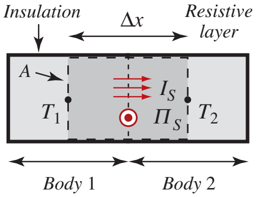

Figure Ex.4.1

The model can be constructed using the entropy or the energy balances for the bodies; remember that the conductor is treated as an element that does not store entropy. Let us use the balance of energy:

$$\begin{aligned} C\dot{T}_1 &= -I_E \quad , \quad T_1(0) = T_{1i} \\ C\dot{T}_2 &= I_E \quad , \quad T_2(0) = T_{2i} \end{aligned}$$

C is the temperature coefficient of energy of a body, and *CdT/dt* is equal to *dE/dt* of a body. The bodies are taken to be identical, with different initial temperatures. The energy current flowing from the hotter to the cooler body is expressed by

$$I_E = \frac{k_E A}{\Delta x}(T_1 - T_2)$$

A is the cross section of the bodies (the surface area where they are touching), k_E is the thermal conductivity, and Δx is a distance which we take to be the distance of the centers of the two bodies. We now divide the differential equations by the temperature coefficients of energy, and then subtract the second from the first. This leads to a differential equation for the difference of temperatures $\Delta T = T_1 - T_2$:

$$\frac{d}{dt}\Delta T = -2\frac{k_E A}{\Delta x C}\Delta T$$

whose solution turns out to be

$$\Delta T = \Delta T_i \exp(-t/\tau) \quad , \quad \tau = \frac{\Delta x C/2}{k_E A}$$

where ΔT_i is the initial temperature difference of the bodies (see Fig. Ex.4.1).

(b) A long bar has an initial temperature distribution with its left half at 400 K and its right half at 200 K. The first of the diagrams (Fig. Ex.4.2, left) depicts the temperatures at evenly spaced points throughout the bar as a function of time (result of an FE computation). The second graph shows the average temperature of the two halves of the bar (circles) and the solution computed according to the result in (a) with Δx equal to half of the length of the bar. (Values are: $k_E = 1$, $C = 5$, $\Delta x = 5$, $A = 1$.) A judicious choice of Δx can make the solutions quite similar, and the rough model can serve as an estimate of what is happening in the bar.

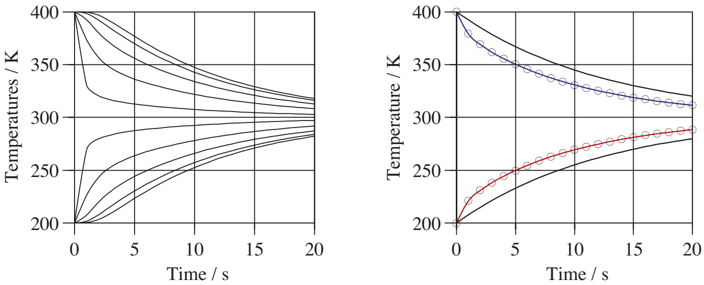

Figure Ex.4.2

(c) The irreversibility is measured in terms of the production of entropy. The rate of generation of entropy is expressed by

$$\Pi_S = I_E\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{k_E A}{\Delta x}\left(T_1 - T_2\right)\frac{T_1 - T_2}{T_1 T_2}$$
$$= \frac{k_E A}{\Delta x}\left(T_1 - T_2\right)^2 \frac{1}{\left(T_f + \Delta T/2\right)\left(T_f - \Delta T/2\right)}$$

If we introduce the solution into this formula, we obtain

$$\Pi_S = \frac{k_E A}{\Delta x}\frac{4\exp\left(-2t/\tau\right)}{4\left(T_f/\Delta T_i\right)^2 - \exp\left(-2t/\tau\right)}$$

Integration of this expression over time (from zero to infinity) leads to[2]

$$S_{prod} = C\ln\left(\frac{4\left(T_f/\Delta T_i\right)^2}{4\left(T_f/\Delta T_i\right)^2 - 1}\right) = C\ln\left(\frac{4T_f^2}{4T_f^2 - \Delta T_i^2}\right) = C\ln\left(\frac{T_f^2}{T_{1i}T_{2i}}\right)$$

The last form is equivalent to the one obtained from thermostatic considerations alone, i.e., by applying balances of entropy and energy to the total process of equilibration of two identical bodies (Chapter 4).

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[2] The solution is obtained from

$$\int \frac{\exp(ax)}{b + c\exp(ax)}dx = \frac{1}{ac}\ln\left(b + c\exp(ax)\right)$$

EXAMPLE 7.5. The flow of heat through the mantle of the Earth.

The total flux of energy from the interior of the Earth through its surface can be estimated from the values of the temperature gradient in the crust and the conductivity with respect to energy. Their values are 0.06 K/m and 1 W/ (K · m), respectively. Assume that the entire flux is conducted from the core at a depth of 3400 km through the solid mantle (the radius of the Earth is 6400 km). Take as an average thermal conductivity the one found for the upper crust. According to these assumptions, how large would the temperature of the core of the Earth be?

SOLUTION: First we have to calculate the energy flux at the surface of the Earth. According to Equ.(7.17) it must be

$$I_{E,th} = 4\pi R^2 k_E \frac{dT}{dr} = 3.1 \cdot 10^{13} \text{ W}$$

R is the radius of the Earth. The energy flux out of the Earth is about 5000 times smaller than the one we receive from the Sun. We have applied Fourier's law, which was motivated for flat geometry. This is certainly allowed in the case of purely radial flow. We need only replace the normal temperature gradient by its radial counterpart. The following development, however, changes because of the differences in geometry.

If we knew the thermal resistance R_E of the Earth's mantle we could easily calculate the temperature difference necessary to conduct this current from the bottom of the mantle up to the surface. Since the conducting body is not flat, the surface area through which conduction is taking place varies constantly. Therefore, let us write Fourier's law in the form

$$\left| I_{E,th} \right| = \frac{dT}{dR_E}$$

with

$$\frac{dR_E}{dr} = \frac{1}{k_E A}$$

This means that we have to calculate the thermal resistance by integration. For a spherical shell with inner and outer radii r_i and r_0, respectively, and with constant k_E we get:

$$R_E = \int_0^{R_E} dR_E = \int_{r_i}^{r_0} \frac{dr}{k_E A} = \frac{1}{4\pi k_E} \int_{r_i}^{r_0} \frac{dr}{r^2} = \frac{1}{4\pi k_E} \left(\frac{1}{r_i} - \frac{1}{r_0} \right)$$

Note that the thermal resistance is of the form given in Equ.(7.20), with $\Delta x = r_0 - r_i$ and $A = 4\pi r_i r_0$. According to Equ.(4.46), the difference of temperatures between the core-mantle boundary and the surface must be

$$\Delta T = R_E I_{E,th} = 4.36 \cdot 10^5 \text{ K}$$

This value is rather far off from the estimated temperature difference of some 3000 K. From seismic measurements we know that the mantle is solid, which limits the temperature below the melting point of rocks. A good number of reasons can be given to explain this huge discrepancy. The value of the conductivity might be wrong. (However, it will not be all that far off.) The entropy flowing out through the surface of the Earth might not come from the core; it might be produced in the mantel and the crust by radioactive decay; this is indeed the case (see Chapter 13). The flow of entropy varies with time; in our case, however, this does not change the result much because of the long time scale. Finally, the entropy might be transported not by conduction but by radiation and convection. This is true as well; it is mostly convection which transports entropy through the mantle, even though the mantle is solid! Over very long time scales, the material of the mantle is deformable and it moves; this process apparently is responsible for continental drift.

7.3 THE NATURE OF HEAT TRANSFER AT A SOLID–FLUID BOUNDARY

Now we will introduce some aspects of heat transfer across interfaces separating different types of bodies. Consider a hot solid body submersed in some fluid. Entropy is conducted through the body to its surface from where it enters the fluid and is carried away convectively. The transport of entropy from the solid to the fluid, or vice-versa, is of interest in the design of heat exchangers, in the loss of heat from a building, in thermal solar collectors, in household appliances, and in many other applications. Another important case is heat transfer between liquids and gases. Just think of the interaction between the Earth's atmosphere and the oceans, which has received much attention recently. Questions concerning the balance of energy and entropy, and of carbon dioxide and other trace gases, are of vital interest in environmental, atmospheric, and oceanographic sciences.

7.3.1 Boundary Layers

For now, let us limit our attention to the flow of entropy from solids to fluids. The transport mechanism is usually a mixture of conduction, convection, and radiation. (The last will be treated in Section 7.4.) Entropy flows through a hot body to its surface from where it somehow enters the fluid. For example, consider a viscous fluid flowing along a flat plate as in Fig. 7.11. The hydrodynamic phenomenon is described by the velocity of the fluid in the vicinity of the plate. The conditions in the undisturbed fluid are given by the free stream values of velocity and temperature far from the plate. Due to viscosity, the speed of flow is reduced to zero at the surface of the body. It is found that the velocity changes in a direction perpendicular to the surface from the value of zero to the free stream velocity further away in the undisturbed flow. The velocity gradient is confined to a thin *hydrodynamic* or *velocity boundary layer* in which all the interesting action takes place (Fig. 7.12a). The thickness of the boundary layer is zero at the leading edge of the plate and it increases with increasing distance along the surface. The boundary layer is defined to extend to points where the velocity has reached 99% of the free stream value. Typically, in the situation described, it has a thickness of the order of only a few millimeters.

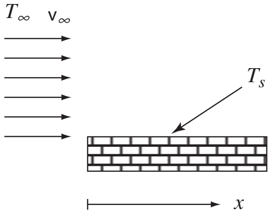


Figure 7.11: A fluid flows past a long flat plate. The fluid has free stream values of velocity and temperature far from the plate. The surface temperature of the solid body is assumed to be constant and different from the free stream value of the fluid. As a result, entropy and energy will be carried across the interface by the combined action of conduction and convection.

Now consider the temperature of the fluid. At the surface of the solid, the fluid is at rest and its temperature is that of the solid surface, which in general, is different from the free stream value. Therefore temperature gradients must develop perpendicularly to the surface; i.e., the temperature changes from the surface value to the free stream value, this time in a thin *thermal boundary layer* (Fig. 7.12b).

Again the thickness of this boundary layer increases along the plate from a value of zero at the leading edge. We can understand the importance of the conditions in the boundary layer for the transport of entropy. At the surface of the solid, entropy is transferred into the fluid in the conductive mode only. This allows us to write the entropy flux density in terms of the conductivity of the fluid and the temperature gradient in the fluid at the surface:

$$j_S = -k_{Sf} \left. \frac{dT}{dy} \right|_{y=0} \qquad \textbf{(7.24)}$$

(see Equ.(7.14)). The index *f* refers to the fluid. Naturally, conditions in the fluid layer change right away, so Equ.(7.24) holds only for the surface ($y = 0$).

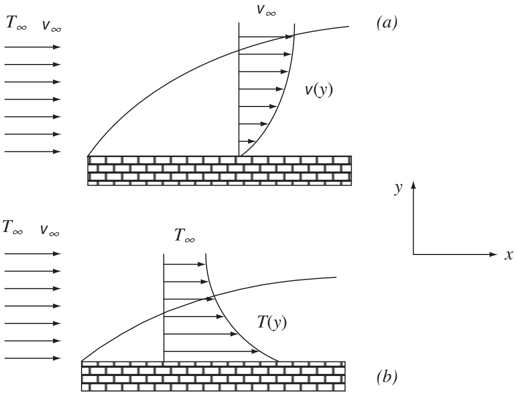


Figure 7.12: Velocity (a) and temperature (b) boundary layers develop at the surface of the solid body. The velocity is zero right at the surface, from where its value increases to the free stream velocity. The distance over which the quantity changes marks the extent of the boundary layer which increases along the plate. The temperature is equal to the surface temperature for $y = 0$. It decreases (or increases) from the surface to obtain the free stream value. The thicknesses of the velocity and temperature boundary layers are not the same.

7.3.2 Convective Heat Transfer Coefficient

Entropy and energy which enter the fluid conductively will be carried away with the flow of matter. The entropy and energy currents crossing the interface must depend in some way upon the physical state of the fluid and the temperatures at the surface of the body as well as far away from it. The process is a rather complex phenomenon. That is why it is commonly described in a strongly simplified manner. The entropy flux density is expressed in terms of the difference of temperatures between the surface of the solid body and the fluid far from the surface, and a coefficient which summarizes the complexity of the physical state of the fluid:

$$j_S\Big|_{y=0} = h_S\left(T_s - T_\infty\right) \tag{7.25}$$

h_S is called the (local) *convective entropy transfer coefficient*, while T_s and T_∞ represent the temperature of the surface and of the undisturbed fluid, respectively. The coefficient depends upon the details of the fluid flow. It has to be either calculated on the basis of a complete hydrodynamic theory, or measured in experiments. The expression in Equ.(7.25) is equal to the entropy flux at the interface, which allows us to equate the flux densities in Equations (7.24) and (7.25). This leads to an expression for the entropy transfer coefficient:

$$h_S = -\frac{k_{Sf}}{T_s - T_\infty}\frac{dT}{dy}\bigg|_{y=0} \tag{7.26}$$

Both the conductivity of the fluid and the temperature difference can be taken to be constant. Therefore, the convective transfer coefficient depends upon the temperature gradient of the fluid at the surface of the solid, which is determined by the conditions in the boundary layer. Experience tells us that a hot body submersed in a flowing medium cools much faster than in a still fluid. Therefore, the rate of transfer of entropy from a solid into a liquid or gas crucially depends upon the state of motion of the fluid. The type of flow plays an important role as well. We have to distinguish between *laminar* and *turbulent* flows on the one hand, and forced and free convection on the other. The rate of entropy transfer is very different in these cases. It is clear that we have not really solved the problem of convective heat transfer; we have simply shifted it to the task of determining the transfer coefficient from a theory combining motion and heat transfer.

The temperature gradient at the surface of the solid obviously diminishes with increasing thickness of the layer, which leads us to conclude that the local value of the transfer coefficient decreases along the plate. The coefficient is often replaced by an average value. In this case we can relate the entire entropy flux to the change of temperature and the *average transfer coefficient* h_{Sa}:

$$I_S\Big|_{y=0} = h_{Sa} A\left(T_s - T_\infty\right) \tag{7.27}$$

A is the total surface of the body. In this simplified form the constitutive law of convective entropy transfer commonly serves as a boundary condition for the conductive transport of entropy through the solid body.

Naturally, the entropy flux varies across the boundary layer. Entropy will be produced in the fluid due to both conduction and viscous friction. These are two of the possible dissipative processes taking place in the general type of fluid considered here.

The exchange of energy with entropy at the interface. The entropy current which is expressed by Equ.(7.27) is carried across the surface of the solid body by conduction alone, so it is possible to give a simple form of the energy flux entering or leaving the solid. In conduction, the entropy and energy currents are related by the local temperature. Therefore the energy flux at the surface is equal to

$$I_{E,th}\Big|_{y=0} = h_a A\left(T_s - T_\infty\right) \tag{7.28}$$

where

$$h_a = T_s h_{Sa} \tag{7.29}$$

is called *heat transfer coefficient*. We need to know the average transfer coefficient for concrete applications. Such values are listed in Table 7.2 for a few situations.

Table 7.2: Heat transfer coefficients with respect to energy [a]

Substance	**Transport mode**	h_a / W · K^{-1}m^{-2}
Air	Free convection	6–30
Air in rooms	Inside wall	8
	Window	8
	Floors and ceilings	6–8
Superheated steam or air	Forced convection	30–300
Oil	Forced convection	60–1800
Water	Forced convection	300–6000
	Boiling	3000–60000
Steam	Condensing	6000–120000

[a] Order of magnitude, including the effect of radiation at the boundary.

From the foregoing we can define conductances or resistances. The expression for an energy flow *conductance* of a convective layer is

$$G_{E,conv} = h_a A \tag{7.30}$$

The inverse of this quantity is the (energy) *resistance*. Corresponding entropy conductances are calculated by dividing G_E by the appropriate temperatures. Once we know how to calculate conductances or resistances of single layers, we can find the overall conductance or resistance for compound layers just as in the case of conduction alone (Equ.(7.22) and Equ.(7.23)).

7.3.3 Overall (Total) Heat Transfer Coefficient

How large is the flux of entropy or energy through the wall of a building or through the insulation of a pipe? Obviously we are dealing with multilayer situations in which both conduction through solids and convection at solid–fluid boundaries occur. This situation was discussed in Chapter 4 (Section 4.6.4 and Fig. 4.44).

Consider heat transfer through a wall of a building. The transfer of energy is described in terms of the total difference of temperatures between the inside and the outside of the building, the surface area A, and an *overall heat transfer coefficient* h_{tot}:

$$I_{E,th} = h_{tot} A\left(T_1 - T_2\right) \tag{7.31}$$

$h_{tot} A$ is the overall conductance which can be calculated exactly as for compound conductive layers (Equ.(7.22) and Equ.(7.23)). Hence, for a *series of layers* (as in Fig. 4.44), the total heat transfer coefficient is

$$\frac{1}{h_{tot}} = \sum_{i=1}^{N} \frac{1}{h_{ai}} + \sum_{j=1}^{M} \frac{\Delta x_j}{k_{Ej}} \tag{7.32}$$

where the Δx_i are the thicknesses of each of the conducting layers which have conductivities k_{Ei}. There are N transition layers and M conductive ones.

QUESTIONS

10. If air is heated inside a room, would you expect heat to reach the walls by conduction through the air or rather by convective mixing of the air in the room?
11. Consider air flowing along a (heated) plate. Why should we expect the convective transfer coefficient to change along the plate (in flow direction?)
12. Consider hot air flowing along a cool plate. What will the temperature layer in the direction of flow look like?
13. If a box is insulated by 10 cm or more of glass fiber, do we still have to take into consideration convective transfer on the outside?
14. Consider hot water inside a thin-walled aluminum can cooling in the environment. Why is the convective transfer coefficient from the outside surface of the can to the air nearly equal to the total transfer coefficient from water to air?
15. What is the (entropy or energy) transfer coefficient for a conductive layer? How does it differ from the transfer coefficient for convection?

EXAMPLE 7.6. Surface temperature of a central heating radiator.

To heat a 100 m^2 apartment in an older not very well insulated building we need 1600 liters of heating oil per year. One liter of oil yields about 36 MJ when burned. Assume that the entire floor of the apartment is used for floor heating, and that the heating is on for one third of the year. (a) What is the average entropy current from the floor to the air? (b) How much warmer than the air will the surface of the floor have to be? Use a floor temperature of 300 K.

SOLUTION: (a) The entropy current is calculated from the energy current which is obtained from the energy delivered by the oil during about 10^7 s. For one square meter, we have

$$j_S = \frac{1}{T_{floor}} \frac{I_E}{A} = \frac{1}{T_{floor}} \frac{E_{e,th}}{A\Delta t} \approx \frac{1600 \cdot 36 \cdot 10^6}{300 \cdot 100 \cdot 10^7} \frac{\text{W}}{\text{K} \cdot \text{m}^2} = 0.20 \frac{\text{W}}{\text{K} \cdot \text{m}^2}$$

(b) The entropy current calculated in (a) must be transferred from the floor to the air. According to Table 7.2, the entropy transfer coefficient from a floor to air is about 8/300 W/($K^2 \cdot m^2$). With Equ.(7.25), we have:

$$\Delta T = \frac{j_S}{h_{Sa}} \approx \frac{0.2}{8/300} \text{K} = 7.5\text{K}$$

EXAMPLE 7.7. Surface temperatures of a single pane window in winter.

Consider a window having a metal frame. The window measures 1.20 m by 2.00 m. The glass has a thickness of 3.0 mm, and a conductivity with respect to energy of 1.0 W/(K·m). Take the convective transfer coefficients inside and outside to be 8.0 W/(K·m^2) and 12.0 W/(K·m^2), respectively. The metal frame is 3.0 cm wide around the window, and 5.0 mm thick. The conductivity is 220 W/(K·m) (aluminum), and the transfer coefficients inside and outside are taken to be 30 W/(K·m^2) and 50 W/(K·m^2), respectively. The temperature on the inside is 20°C; on the outside it is – 10°C. (a) What are the temperatures of a single pane window inside and outside in winter? (b) Calculate the flux of energy through the window if it has a metal frame. (c) How large is the total transfer coefficient of the window?

SOLUTION: (a) The energy flux through the glass is given by Equations (7.31) and (7.32):

$$\begin{aligned} I_{E,th} &= h_{tot} A \Delta T \\ &= \left[\frac{1}{8.0} + \frac{0.0030}{1.0} + \frac{1}{12.0} \right]^{-1} 2.4 \cdot 30 \text{ W} = 340 \text{ W} \end{aligned}$$

We use this value to calculate the temperature drop from the inside to the surface of the window:

$$\Delta T = \frac{I_{E,th}}{h_{a1} A} = \frac{340}{8.0 \cdot 2.4} \text{K} = 17.7\text{K}$$

which makes the temperature on the inside of the window 2°C. The same consideration for the thermal boundary layer outside delivers a temperature drop of 11.8 K. This means that the change of temperature through the glass is very small, and the outside surface has approximately the same temperature as the surface on the inside.

(b) The metal frame adds to the energy current. (It is in parallel with the window pane.) The surface area of the frame is roughly 0.19 m^2. Just as above, we calculate the energy current:

$$I_{E,th} = \left[\frac{1}{30} + \frac{0.0050}{220} + \frac{1}{50} \right]^{-1} 0.19 \cdot 30\text{W} = 110\text{W}$$

The total energy current turns out to be 450 W which is very large. Note that the metal frame has a strong influence despite its small surface area.

(c) The total transfer coefficient is given by Equ.(7.32):

$$h_{tot} = \frac{I_{E,th}}{A\Delta T} = \frac{450}{2.6 \cdot 30}\frac{\text{W}}{\text{K} \cdot \text{m}^2} = 5.8\frac{\text{W}}{\text{K} \cdot \text{m}^2}$$

Good windows achieve a much smaller value of this coefficient (by as much as a factor of 10).

EXAMPLE 7.8. A surprising effect of insulation.

A metal pipe is to be insulated. It is found that, at least in principle, the insulation can have the opposite effect of what we would expect: the current of heat through the walls and the insulation of the pipe increases! How is this possible? Determine the conditions for the maximum heat flow.

SOLUTION: The thermal resistance of the insulation is made up of the resistance of the layer of insulation itself, and of the effect of convection at its surface. While the resistance of the insulating cylindrical shell grows with increasing thickness, the resistance due to the thermal boundary layer decreases because of the increase of surface area. There will be a minimum value of the total resistance at a certain outer radius of the insulation, depending on the material properties.

First we need an expression for the thermal resistance of a cylindrical shell (Fig. Ex.8). We proceed as in the case of a spherical shell (Example 7.5):

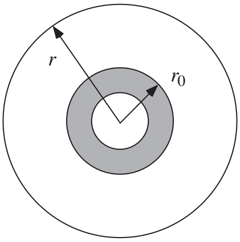


Figure Ex.8

$$R_E = \int_{r_0}^{r} \frac{1}{2\pi k_E L}\frac{dr}{r} = \frac{1}{2\pi k_E L}\ln\left(\frac{r}{r_0}\right)$$

The total resistance of insulation and boundary layer is

$$R_{tot} = R_{insulation} + R_{conv} = \frac{1}{2\pi k_E L}\ln\left(\frac{r}{r_0}\right) + \frac{1}{2\pi h_a L r}$$

Its minimum is found by setting its derivative with respect to the radial variable equal to zero. We obtain

$$r_{min} = k_E / h_a$$

The value of r for which the thermal energy current becomes largest does not depend upon the radius of the pipe. However, r_0 certainly must be smaller than the quantity just calculated. For normal values of the constitutive quantities, the pipe (and the insulation) must be rather thin. One might imagine the effect to play a role, for example, when ice starts to build up around thin branches or fibres in plants. An interesting suggestion has been made concerning the improvement of heat transfer through the air–water or air–air heat exchanger of a heat pump. At the cold end of the device, ice tends to build up at the surface, normally reducing the effectiveness of the pump. The geometry of the device could possibly be such that frost building up at its surface would lead to an increase of the rate of heat transfer.

EXAMPLE 7.9. Formation of ice on the surface of a lake.

Ice forms on the surface of a lake while the temperature of the air is – 10°C. How long does it take from the time ice begins to form for the sheet to reach a thickness of 20 cm? Take the temperature of the air to be constant. The convective transfer coefficient from ice to the air is 10 W/

(K · m^2). The conductivity with respect to energy of ice is 2.2 W/(K · m). Neglect the transfer from the water to the ice.

SOLUTION: For ice to form at the surface of the lake, the water must have reached a temperature of 0°C. Heat flows from the water into the air, first directly, and later through the ice; therefore water will freeze. If we can calculate the rate of formation of ice, we can determine the rate at which the thickness of the sheet grows.

The equation for the current of entropy leaving the water as it turns into ice is Equ.(5.2) written for the mass of the water:

$$I_S = l_{f,ice} \Pi_{m,water}$$

$l_{f,ice}$ is the specific latent entropy of fusion of ice (Table 5.1). The rate of production (destruction) of mass of water equals the negative of the rate of production of mass of ice which is equal to the rate of change of mass of ice:

$$\frac{dm_{ice}}{dt} = -\Pi_{m,water}$$

Combining these rules leads to

$$\frac{dm_{ice}}{dt} = -\frac{I_S}{l_{f,ice}}$$

The current is determined by the rules discussed in this section:

$$I_S = \frac{1}{T_{water}} \frac{\Delta T}{R_E} = \frac{1}{T_{water}} \left(T_{air} - T_{water}\right) A \left[\frac{1}{h_a} + \frac{x}{k_E}\right]^{-1}$$

x is the instantaneous thickness of the ice sheet. If ice has not formed yet, the total transfer coefficient is the convective transfer coefficient alone. Furthermore, we can express the rate of change of the mass of the ice in terms of the rate of change of its thickness:

$$\frac{dm}{dt} = \rho_{ice} A \frac{dx}{dt}$$

In summary we get the following differential equation for the thickness of the sheet of ice:

$$\rho_{ice} A \frac{dx}{dt} = -\frac{1}{l_{f,ice}} \frac{1}{T_{water}} \left(T_{air} - T_{water}\right) A \left[\frac{1}{h_a} + \frac{x}{k_E}\right]^{-1}$$

Separating the variables and integrating, we obtain

$$\int_0^t dt = -\frac{l_{f,ice} T_{water} \rho_{ice}}{h_a k_E \left(T_{air} - T_{water}\right)} \int_0^x \left(k_E + h_a x\right) dx$$

For the sheet of ice to grow to a thickness of 0.20 m, we have to wait for a time

$$\begin{aligned} t &= \frac{l_{f,ice} T_{water} \rho_{ice}}{h_a k_E \left(T_{water} - T_{air}\right)} \frac{1}{2h_a} \left[\left(k_E + h_a x\right)^2 - k_E^2\right] \\ &= \frac{1220 \cdot 273 \cdot 920 \cdot \left(4.2^2 - 2.2^2\right)}{10 \cdot 2.2 \cdot (10 - 0) \cdot 2.0 \cdot 10} \text{s} = 8.8 \cdot 10^5 \text{s} \end{aligned}$$

This corresponds to about 10 days, which seems to be a pretty reasonable time span. It decreases noticeably if h_a increases because of stronger winds.

EXAMPLE 7.10. Cooling hot water in cold thick-walled container.

Hot water is poured into a thick walled cylindrical PVC container (Fig. Ex.10, left) that is well sealed at the top and at the bottom. The water is stirred continuously by a magnetic stirrer. As the water cools, temperatures of the water, the outside surface of the container, and the air are measured as functions of time (Fig. Ex.10.1, center; right: enlargement of the initial phase). The temperature of the air is almost constant.

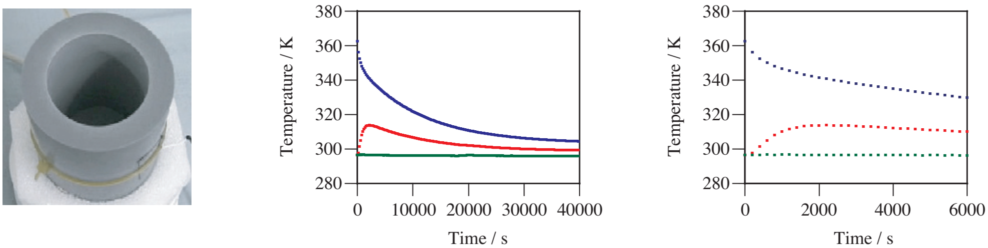


Figure Ex.10.1

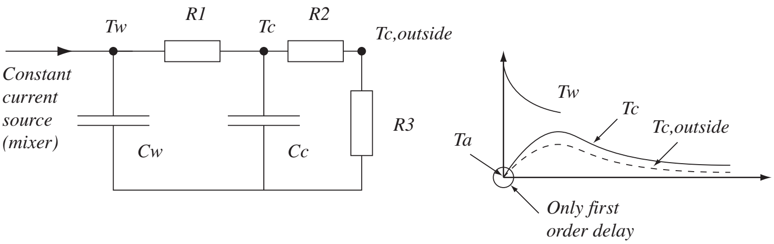
Experimental data: Power of the mixer: 1.0 W; mass of water: 0.30 kg; height of PVC cylinder: 0.105 m; inner radius: 3.00 cm; outer radius: 4.65 cm; density of PVC: 1400 kg/m^3; convective transfer coefficient PVC to air: 12 W/(K·m^2); the convective transfer coefficient from water to PVC is much higher.

(a) Explain the temperature-time diagram in words (note: the temperature of the water initially drops faster than would be expected from a simple exponential decay; the temperature of the outside surface of the container rises with a delay, etc.). (b) Think of the simplest possible model that might explain these observations. Sketch an electric circuit that represents your model. Sketch the corresponding diagram of a dynamical model. (Use the energy representation for your model.) (c) Formulate all equations for your model (without calculating conductances in detail). (d) Use experimental data to estimate the thermal properties of PVC (conductivity and specific heat).

SOLUTION: (a) T_w decreases since water loses entropy to the container. T_c increases first because of high gain of entropy. Then the container loses more and more entropy to the environment: T_c goes down. T_w decreases faster at the beginning than later because the container gets warmer. T_c(outside surface) has a second order delay since entropy takes time to flow through the wall. T_w and T_c stay above T_a because of entropy production by mixer.

(b) The simplest possible model has a capacitor each for water and for the container (Fig. Ex.10.2, left; with only a capacitor for water, there is no independent temperature for the container wall to compute). Voltages represent temperatures of uniform bodies; so T_w is the temperature of the water, T_c is the temperature at the center of the container wall.

Figure Ex.10.2



The resistor between the capacitors represents the transitional layers from the water to the center of the PVC wall. R_2 symbolizes the conductive resistance from the center of the wall to its outer surface, whereas R_3 is used for the convective transition from the surface to the air. From what we know of simple electric or hydraulic *RC* models (Chapter 1), the expected behavior of the temperatures is as in Fig. Ex.10.2, right. Gross features of the real behavior are there, but the delay in the temperature of the outside surface of the wall is absent. We need a better model with the wall divided into two or morel (radial) elements (Fig. Ex.10.3, top). The bottom part of Fig. Ex.10.3 shows a diagram of a dynamical model representing the circuit. In this model, T_{C2} and $T_{C,outside}$ show the expected delay.

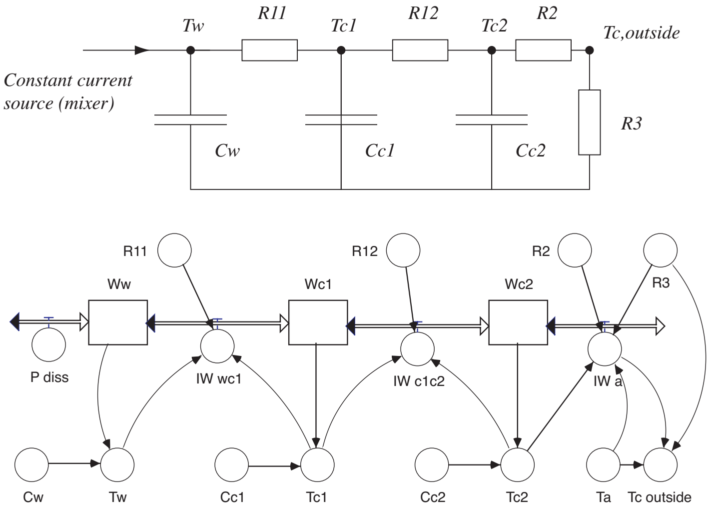


Figure Ex.10.3

(c) The simpler two-node model suffices for demonstrating the physical and mathematical structure. Its equations of balance (of energy) are:

$$\frac{dE_w}{dt} = \mathcal{P}_{mix} - I_{E,wc} \quad , \quad \frac{dE_c}{dt} = I_{E,wc} - I_{E,ca}$$

With capacitive relations

$$T_w = \frac{1}{C_w} E_w \quad , \quad T_c = \frac{1}{C_c} E_c$$

and flow laws

$$I_{E,wc} = \frac{1}{R_1}\left(T_w - T_c\right) \quad , \quad I_{E,ca} = \frac{1}{R_2 + R_3}\left(T_c - T_a\right)$$

the model is complete (except for initial conditions). The surface temperature of the container can be calculated from the results of this model:

$$T_{c,outside} = T_a + R_3 I_{E,ca}$$

(d) It is possible to formulate conditions for the missing material properties of PVC, i.e., its conductivity and its specific heat. The conditions are obtained from considerations of special circumstances. Let us start with the steady state which obtains after a long time (data in Fig. Ex.10.1, center):

$$I_E(to\ air) = I_E(through\ wall) = \mathcal{P}_{mix}$$

The energy current through the wall can be expressed as follows:

$$I_E(through\ wall) = k_{Wall}\frac{A_{Wall}}{\Delta x_{Wall}}\Delta T$$

Let us assume that the wall is flat. Since we know this current from steady-state conditions (it is equal to the power of the mixer), we can calculate the conductivity of PVC:

$$k_{Wall} = \frac{I_E \Delta x}{A\,\Delta T} = \frac{1.0 \cdot 0.0165}{2\pi \cdot 0.040 \cdot 0.105 \cdot 4.3}\frac{\mathrm{W}}{\mathrm{K \cdot m}} \approx 0.15\frac{\mathrm{W}}{\mathrm{K \cdot m}}$$

The capacitance (specific heat) of the container is found as follows. Consider the balance of energy for container for a period of time from 0 s to 200 s:

$$\begin{aligned}
\Delta E_c &= \left|\Delta E_{Water}\right| - \left|E_{Loss\ from\ wall}\right| \\
&= mc\left|\Delta T_{water}\right| - A_c h_{loss}\left|\Delta \overline{T}_{surfac\,to\,air}\right|\Delta t \\
&= 0.30 \cdot 4200 \cdot 21\,\mathrm{J} - 2\pi \cdot 0.0465 \cdot 0.105\,\mathrm{m}^2 \cdot 12\frac{\mathrm{W}}{\mathrm{K \cdot m^2}} \cdot 13\,\mathrm{K} \cdot 2000\,\mathrm{s} \\
&= 17000\,\mathrm{J}
\end{aligned}$$

In the first 2000 s, the temperature of the water (0.30 kg) drops by about 21 K. The energy loss of the wall is calculated from its average surface temperature relative to the ambient, its surface area and the convective transfer coefficient. The specific heat is related to the change of energy of the body:

$$\Delta E_c = c_c m_c \Delta T_c \qquad \Delta T_c \approx 30\mathrm{K}$$

$$c_c = \frac{\Delta E}{m_c \Delta T_c} = \frac{17000\,\mathrm{J}}{\rho_{\mathrm{PVC}}\pi\left(0.0465^2 - 0.030^2\right) \cdot 0.105\mathrm{m}^3 \cdot 30\mathrm{K}} \approx 1000\frac{\mathrm{J}}{\mathrm{K \cdot kg}}$$

ΔT_c is estimated as follows. Initially, T_c is equal to ambient temperature (25°C). At t = 2000 s, the outside of the container is 41°C, on the inside it is nearly as warm as the water (69°C). This gives the container an average temperature of 55°C at t = 2000 s. These results agree rather well with values from tables.

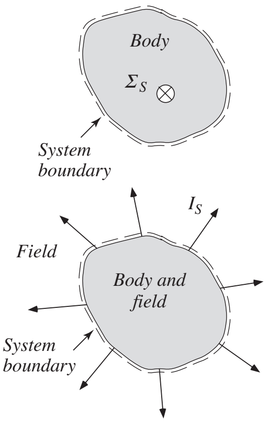


Figure 7.13: Radiation from the surface of an opaque body. There is a constant exchange of radiation between matter and field in the space occupied by both (top). Outside the body we simply see the radiation which is traveling through the field. The radiation seen outside effectively comes from a very thin layer at the surface of the material body (bottom).

7.4 BLACKBODY RADIATION FROM OPAQUE SURFACES

Next let us consider how a body radiates heat into its surroundings. Even though radiation is a rather complex phenomenon, one case can be treated fairly simply—the emission (and absorption) of radiation by an opaque body. Emission and absorption are volumetric processes as discussed in Section 7.1; still the emission from an opaque body looks like the flow of radiation from a surface. Let me describe briefly how this happens.

A warm body emits radiation to the field occupying the same region, leading to a sink of radiation with respect to the body (and a source with respect to the field). Radiative transport through the field inside the system boundary in Fig. 7.13 is rather complicated. Radiation is emitted and reabsorbed constantly at such rates that the net effect is a flow of heat from hotter to cooler points. Since the body is assumed to be (just about) opaque to the radiation, what we see outside the system must originate from a relatively thin layer at the surface of the body. Outside the space occupied by matter, however, we have a simpler situation. There, radiation is traveling away from the region where it was emitted. If we surround the system by a surface, radiation effectively flows through the field through this boundary.

7.4.1 Hemispherical emission by blackbody surfaces

We are interested in an expression for the fluxes of entropy and energy from the surface of a body which is emitting radiation to its surroundings. In this section, we will discuss only the simplest cases, starting with radiation from the surfaces of *black bodies*. A black body is defined as one which absorbs all the radiation falling upon it. In Section 5.4, we studied blackbody radiation inside a cavity. On the basis of what is known about such radiation, we can motivate the form of the law for radiative transfer from the surface of a body such as the one in Fig. 7.14. If the surface layers of an opaque body have properties which lead to blackbody radiation, the radiation will be the same as if it had originated from a cavity deep inside the system. Since entropy and energy are carried away by radiation, their flux densities must be related to their (volume) densities inside the radiation field. From Section 5.4, Equations (5.83) and (5.86), we know that the density of entropy of blackbody radiation is proportional to the third power of its temperature, while the energy density depends upon the fourth power of the temperature. For this reason the rates at which these quantities flow with radiation from the surface of a body have the same dependence on temperature. It is customary to introduce the *hemispherical rate of emission of energy of a black body* or the *hemispherical emissive power of a black body* $\mathcal{E}_b$, which is defined as the amount of energy emitted by the surface of a black body per unit time and *per unit surface area*. We expect a law of the form:

$$\mathcal{E}_b = \sigma T^4 \tag{7.33}$$

The index b denotes black body radiation. Its counterpart, the *rate of emission of entropy*, $\mathcal{E}_{Sb}$, is expressed by

$$\mathcal{E}_{Sb} = \frac{4}{3}\sigma T^3 \tag{7.34}$$

This is, again, valid for blackbody radiation only. These expressions will be derived in Chapter 12. The constant σ introduced in these relations is called the *Stefan-Boltzmann constant*, and has the value $5.67 \cdot 10^{-8}$ W/(m$^2 \cdot$K^4). $\mathcal{E}_b$ has units W/m^2 and the units of $\mathcal{E}_{Sb}$ are W/K/m^2.

The rates of emission introduced here look very much like current densities that are used to describe the distribution of flows over a surface (see Equ.(7.13)). However, they are not real current densities since the type of transport is rather different from what we know from conduction (i.e., diffusion). In diffusion of charge, substances, or entropy through a material, the fluidlike quantity is transported at one point only in a single direction. Radiation, however, travels in all direction from a point (Fig. 7.14, bottom). Radiation can penetrate itself, meaning it can and will cross through a point in a field in and from all directions. Still, we can integrate the contributions of the transport of, say, entropy or energy over all directions and so obtain the total transfer of the quantity (per unit time and per unit area). This is what the rates of emission in Equ.(7.33) and Equ.(7.34) represent. When this does not cause a confusion, I will call these quantities current densities (fluxes per unit area).

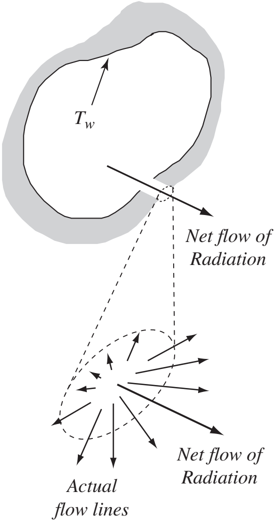


Figure 7.14: Blackbody radiation from the surface layers of an opaque blackbody is the same as that originating from the inside of a cavity in a body (Section 5.4).

If the rates of emission (the current densities) are constant over a surface, the currents of entropy and energy from the entire surface of a body are obtained simply by multiplying the emission rates by the surface area A:

$$I_{S,rad} = -\frac{4}{3}\sigma A T^3 \tag{7.35}$$

$$I_{E,rad} = -\sigma A T^4 \tag{7.36}$$

You should notice an important point: the relation between currents (fluxes) of entropy and of energy, which applies to the heating or cooling of a body (Equ.(4.21)), does not hold in the case of radiative fluxes through the radiation field. Heating and cooling of the material body, however, take the form of sources and sinks of entropy and energy for which the simple and direct relation between source rates of entropy and energy holds; see Equ.(7.41).

Net radiative energy flux for a black body radiator. In general, the expressions in Equations (7.35) and (7.36) are not the net fluxes, since the body might absorb heat from another piece of matter radiating towards it. It is instructive to derive the net energy flux for a black body totally surrounded by another black body at a different temperature T_w (such as the small piece of matter in the cavity in Fig. 7.15). Remember that the radiation field set up by the walls of the cavity is isotropic and the same at every point inside. This means that a point at the surface of the small body surrounded by the walls sees blackbody radiation coming at it at the same rate from all directions. Therefore the amount of energy per second and per unit surface area radiated toward, i.e., incident upon the body is

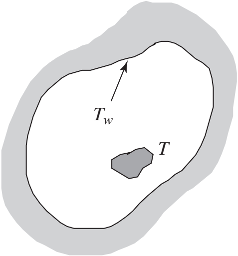


Figure 7.15: A cavity serves as a container of blackbody radiation. The walls are at a temperature T_w, while the small body inside the cavity has a temperature T.

$$\mathcal{G} = \sigma T_w^4 \tag{7.37}$$

$\mathcal{G}$ is called the *irradiance* of the surface. Since a black body absorbs all the radiation falling upon its surface, the net flux of energy with respect to the chunk of matter inside the cavity is given by

$$I_{E,rad,net} = -\sigma A\left[T^4 - T_w^4\right] \tag{7.38}$$

which is the difference between the rates of emission and absorption, i.e., the difference between (7.33) and (7.37). This result will be extended to bodies other than black bodies in Section 7.4.4.

7.4.2 Cooling and Heating of Bodies by Emission and Absorption

As discussed in Section 7.1.4, bodies can emit and absorb radiation. These processes are the result of the interaction of bodies and fields which occupy the same region of space. Therefore, emission and absorption are volumetric phenomena calling for source rates for their formal description. (This discussion could be extended to surfaces if we consider a thin layer around a body absorbing and emitting radiation. We can also extend the formalism by introducing absorption and emission rates per unit surface area.) Here, I will motivate the relationship between the source rates and the rates of production of entropy on the one hand, and the source rates of energy accompanying the processes on the other.

Take the model of a uniform body at temperature T. For the sake of argument, let the body emit entropy and energy to the field occupying the same region of space. (The reasoning also applies to the case of absorption of radiation.) The rates of emission of these two quantities are equal to the rates of change of the entropy and energy of the body if there are no other modes of transfer present:

$$\dot{S} = \Sigma_S \tag{7.39}$$

$$\dot{E} = \Sigma_E \tag{7.40}$$

Remember that processes are reversible in the model of uniform processes. Since the rates of change are related by the Gibbs Fundamental Form for a simple body (see, for example, Equ.(4.35)), the rates of emission satisfy the equation

$$\Sigma_E = T\,\Sigma_S \tag{7.41}$$

which means that the rate of emission of entropy to the field inside the system is equal to the rate of energy emitted divided by the temperature of the body. This result holds for the chunk of matter occupying the region of space in Fig. 7.16. It neglects the fact that entropy is produced as a result of the emission (and absorption) of radiation. However, as far as the body is concerned, this point is immaterial; it does not affect the balance of entropy for the chunk of matter, since our model associates the irreversibility with an additional element between the body and the field (see Fig. 7.6). For the body, emission of heat to a field has the same effect as cooling by conduction as a result of direct contact of a uniform body with its surroundings.

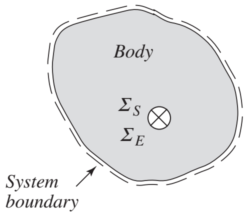


Figure 7.16: A material body and a radiation field occupy the same region of space (only the body is shown). Emission of radiation means that the body loses entropy and energy (and other quantities) at every point inside the field. In this view, the body and field are two separate physical systems.

We should be interested in the rate of production of entropy as a result of the emission or the absorption of radiation. If the processes of emission and absorption are irreversible, the source rates of entropy for the body and the field are not the same. We have expressed this point in Equ.(7.8):

$$\Sigma_S = -\Sigma_{S,field} + \Pi_S \tag{7.42}$$

Together with Equ.(7.41), we can express this in the form valid for the source rate of energy:

$$\Sigma_E = T\left(-\Sigma_{S,field} + \Pi_S\right) \tag{7.43}$$

Consider the case of no entropy being supplied by radiation which is absorbed by a body. Under these circumstances, all the entropy leading to the heating of the body must have been produced, the process being completely irreversible. Put differently, all the energy supplied to the body via the field has been dissipated, and Equ.(7.43) is formally equivalent to the expression for the relationship between the rate at which energy is dissipated and entropy is generated (see Equ.(4.23) of Chapter 4).

In summary, we may interpret the results of emission and absorption of entropy in terms of the cooling or heating of bodies. The only difference from the case treated so far, i.e., heating by conductive surface currents, is that we have to deal with source rates of entropy and energy, Equ.(7.41), instead of fluxes (Equ.(4.21) of Chapter 4). In this model, irreversibility is associated with an extra element placed between the field and the body (Fig. 7.6).

7.4.3 Emission, Absorption, and the Production of Entropy

Irreversibility of emission. Next, we should discuss the rate of production of entropy in the emission and absorption of radiation. Consider the case of emission: the rate at which entropy is emitted by the body to the field is smaller than the rate at which it flows away from the surface of the body (Fig. 7.13). This can be shown quite easily. Consider the model of a uniform body at temperature T for which

$$\Sigma_E = T\Sigma_s \tag{7.44}$$

On the other hand, the flux of entropy through the field at the surface of the body is four-thirds this quantity; see Equations (7.35) and (7.36):

$$I_{S,rad} = \frac{4}{3}\frac{I_{E,rad}}{T} = \frac{4}{3}\frac{\Sigma_E}{T}$$

or

$$I_{S,rad} = \frac{4}{3}\Sigma_S \tag{7.45}$$

We have to conclude that more entropy leaves the space occupied by the body than has been emitted by the body to the field. Therefore, entropy must have been produced in the volume occupied by radiating matter. In the same manner, we can prove that it is impossible for a body to just absorb entropy from a source at the same temperature. Entropy would have to be destroyed, which we know to be impossible. Therefore, it is impossible for a body to absorb entropy at the same temperature without emitting entropy at the same time.

Irreversibility of emission and absorption of two interacting bodies. Consider now the example of combined emission and absorption in a quantitative manner. Take two bodies having geometries such as in Fig. 7.15: the walls of a cavity completely surround a smaller body. Assume both surfaces to be black bodies. Let the smaller body be the hotter one, with temperature T_1 and surface area A. Then the net flux of energy from the smaller to the larger surface is given by Equ.(7.38) where T_2 is the temperature of the enclosure. Now we can compute the rate of production of entropy in the two radiative interfaces between bodies and field (as in Fig. 7.6) combined. With the help of Equ.(7.43) we find that

$$\Pi_S = \Pi_{S1} + \Pi_{S2} = \frac{1}{T_1}\Sigma_{E1} + \Sigma_{S,field1} + \frac{1}{T_2}\Sigma_{E2} + \Sigma_{S,field2}$$

The entropy emitted by one body to the field travels through the field and disappears from the field at the location of the second body, so the source rates for the field cancel, so we have

$$\Pi_S = \Sigma_{E1}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{7.46}$$

Σ_{E1} corresponds to the flux of energy with respect to body 1. This expression is larger than zero since, if $T_1 > T_2$ (Σ_{E1} is negative). The flux of energy will be calculated according to Equ.(7.38) which transforms the production rate of entropy into

$$\begin{aligned}\Pi_S &= \frac{\sigma A}{T_1 T_2}\left(T_1 - T_2\right)\left(T_1^4 - T_2^4\right) \\ &= \frac{\sigma A}{T_1 T_2}\left(T_1 - T_2\right)\left(T_1^2 - T_2^2\right)\left(T_1^2 + T_2^2\right) \\ &= \frac{\sigma A}{T_1 T_2}\left(T_1 - T_2\right)^2\left(T_1 + T_2\right)\left(T_1^2 + T_2^2\right)\end{aligned} \tag{7.47}$$

This expression is larger than zero as long as one of the bodies is hotter than the other and it vanishes if they have the same hotness. Therefore, it does not matter which of the bodies we assume to possess the higher temperature. Emission and absorption of entropy by bodies at different temperatures is necessarily dissipative. We could have performed the computation of the balance of entropy for each of the bodies separately. Using the result for one of them, you can convince yourself that the particular statements made above regarding the irreversibility of emission and the impossibility of absorption without simultaneous emission are correct.

The irreversibility of radiative processes is not limited to the absorption and emission of (blackbody) radiation. Conversion of monochromatic radiation into blackbody radiation and the scattering of radiation have to be added to the list of irreversible processes. The fact that irreversibility necessarily accompanies radiative transfer is of importance for power engineering (see Chapters 9, 15, and 16).

A surface in the light of the Sun. Now consider a particularly relevant case, that of (the surface of) a black body at temperature T in the light of the Sun (Fig. 7.17). Entropy flows with solar radiation toward this surface and, since the body is a black radiator, is completely absorbed. Because of this process of absorption, there is an entropy production rate of Π_{S1}. Let $\mathcal{G}$ be the irradiance of the surface. Solar radiation is nearly black body radiation, so the entropy current incident upon the body of surface area A is

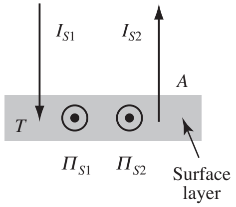


Figure 7.17: Entropy fluxes and entropy production rates for a surface layer of a body in the light of the Sun.

$$I_{S1} = \frac{4}{3} A \frac{\mathcal{G}}{T_{sun}} \tag{7.48}$$

This results from Equations (7.35) and (7.36). T_{sun} is the temperature of the surface of the Sun that emits the radiation which we receive; at the same time this is the temperature of the radiation (see Chapters 12 and 16). If the body only absorbed light, the balance of entropy would be

$$\dot{S} = I_{S1} + \Pi_{S1}$$

so the entropy production rate due to absorption equals

$$\Pi_{S1} = \dot{S} - I_{S1} = \frac{1}{T} I_{E,rad1} - I_{S1} = \frac{1}{T} A\mathcal{G} - I_{S1} = \frac{1}{T} A\mathcal{G} - \frac{4}{3} A \frac{\mathcal{G}}{T_{sun}}$$

The last step is a consequence of Equ.(7.48). We arrive at

$$\Pi_{S1} = \frac{1}{T T_{sun}}\left(T_{sun} - \frac{4}{3} T\right) A\mathcal{G} \tag{7.49}$$

for the production rate of entropy due to absorption of sunlight. Note that this expression becomes negative if T approaches T_{sun}. This tells us that we are not allowed to just consider absorption of radiation by a body; we always have to add entropy production due to emission. (For the case of Sun and Earth, there is no problem since the surface temperature of our planet is so much lower than that of the Sun.)

Since the body is warm at temperature T, it emits an entropy current equal to

$$I_{S2} = -A\sigma\frac{4}{3}T^3 \tag{7.50}$$

Equ.(7.45) tells us that a quarter of this current comes from entropy produced (and not from entropy emitted):

$$\Pi_{S2} = \frac{1}{3}A\sigma T^3 \tag{7.51}$$

The total entropy production rate allows us to make an interesting observation. Summing up the contributions from absorption and emission and setting $T = T_{sun}$, yields

$$\Pi_S = \frac{1}{3}A\sigma T_{sun}^3 - \frac{1}{3}\frac{1}{T_{sun}}A\mathcal{G}$$

which is equal to zero since there is no net exchange of radiation between the Sun and the Earth (with both at T_{sun}). If we accept this, we see that $\mathcal{G}$ must be equal to $\sigma T_{sun}{}^4$, meaning we can bring a body to T_{sun} if the incoming radiation has the intensity of sunlight at the surface of the Sun (which we can get by concentrating the Sun's light).

7.4.4 Radiative Properties of Gray Surfaces

So far we have limited ourselves to the case of blackbody radiation. We should now take a closer look at the emission and absorption of heat from surfaces not having blackbody properties. Since a black surface was defined as one which absorbs all incident radiation, we will now be concerned with *gray* surfaces, which absorb only a fraction thereof.

The absorptivity of gray surfaces. To describe the absorptive properties of a surface we need two quantities. The first was introduced above—the *irradiance* $\mathcal{G}$ which measures the total flow of energy incident on a surface per unit area. We need the *rate of absorption of energy per unit area* abbreviated by $\mathcal{A}$. If $\mathcal{A}$ equals $\mathcal{G}$, the surface is a perfect absorber; if it is smaller than $\mathcal{G}$, the surface is said to be gray. We introduce the *absorptivity* a, the ratio of rate of absorption and irradiance, so

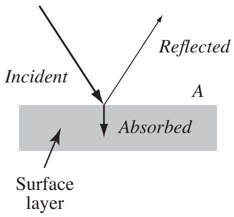


Figure 7.18: Incident ray, absorption and reflection.

$$\mathcal{A} = a\mathcal{G} \tag{7.52}$$

For a black body $a = 1$. Sometimes, the *reflectivity* ρ of an opaque surface is introduced in place of the absorptivity. The energy not absorbed is reflected (Fig. 7.18), which means that the reflectivity and the absorptivity are related by

$$\rho = 1 - a \tag{7.53}$$

Kirchhoff's Law. The interesting question now concerns the emissivity of nonblack surfaces. How does it compare to blackbody radiation? Let us once more consider the radiation inside a cavity. Since the field in the cavity is that of blackbody radiation, the irradiance in this enclosed space is the emissive power of a black body having the temperature of the walls:

$$\mathcal{G} = \mathcal{E}_b \tag{7.54}$$

In other words, the irradiance is the hemispherical power in a blackbody field, Equ.(7.33). Whether the walls are black surfaces does not matter. If they are not, the combination of emittance and reflectance still leads to radiation with blackbody properties. This is the reason why the radiation in a cavity is called *blackbody radiation*. Since the material of which the walls of the cavity are made does not play a role, the only factor determining the radiation in the cavity is the temperature of the walls.

An arbitrary body with absorptivity a is now introduced into the cavity (Fig. 7.19). After some time, stationary conditions will have been reached, the temperature of the small body will be the temperature of radiation in the cavity, and the emissive power of the body will be the fraction of the irradiance absorbed by the body. Since the radiation in the cavity is that of a black body, the emissive power of the body inside the cavity must equal the product of absorptivity and blackbody emissive power:

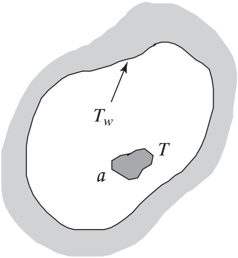


Figure 7.19: A body in a black body radiation field of the cavity. Its surface has an absorptivity equal to a.

$$\mathcal{E} = a\mathcal{E}_b \tag{7.55}$$

This is a form of *Kirchhoff's law*. It states that *the emissive power of a body is a fraction of the emissive power of a black body at the same temperature, where the fraction is the absorptivity*.

If we introduce the *emissivity* e of the body as the fraction of the emissive power of a black body at the same temperature,

$$\mathcal{E} = e\mathcal{E}_b \tag{7.56}$$

we can state Kirchhoff's law by saying that *the emissivity is equal to the absorptivity*. (This statement has to be qualified: they are equal at the same frequency of light; see Section 7.4.6.) Values of the absorptivity (or emissivity) of some materials are listed in Table 7.3. In general, they depend upon the temperature of the surface (Fig. 7.20).

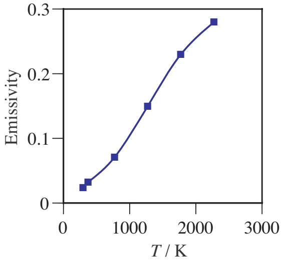


Figure 7.20: Emissivity of tungsten, as a function of temperature.

The net radiant flux for a gray body surrounded by blackbody radiation. If the small body in the cavity has a different temperature, then the rate at which energy is absorbed by the body is not equal to the rate at which it is emitted. The net source rate of radiant energy is calculated to be

$$I_{E,rad} = -A\left(\mathcal{E} - a\mathcal{G}\right) \tag{7.57}$$

A is the surface area of the body in the cavity. Since the emissive power is given by Kirchhoff's law, and since the irradiance in the cavity is equal to the emittance of the walls, we ultimately obtain the following expression for the flux of radiant energy from the surface of the body at temperature T irradiated from a distant surface at temperature T_w which completely surrounds it:

$$I_{E,rad} = -aA\left[\mathcal{E}_b(T) - \mathcal{E}_b(T_w)\right] \tag{7.58}$$

The rate is the difference between the emission and absorption rates as calculated for a blackbody surface, multiplied by the absorptivity of the surface. The blackbody emissive power is the same as that given by Equ.(7.55). In summary, the laws stated here allow us to calculate the flux from a surface area *A* which has a temperature *T*, and which is subject to radiation from surroundings at a temperature T_w:

$$I_{E,rad} = -eA\sigma\left(T^4 - T_w^4\right) \tag{7.59}$$

(the absorptivity has been replaced by the emissivity). Remember that this equation holds only for the particular geometry used in the example: the body is completely surrounded by the walls of the cavity (actually, a large space serves the same purpose; the condition is simply that the radiation of the body is not reflected back). As a result, all the radiation emitted by the walls will be incident upon the body and vice versa. For different geometries, where only part of the radiation emitted by either of the bodies strikes the other surface, the result is much more complicated. In such cases, it is customary to write the result in just about the same form with an additional factor (called the *shape factor*) taking care of the difference (Chapter 12).

Table 7.3: Emissivities and solar absorptivities

Substance		**Emissivity**[a] e	**Absorptivity for solar radiation** a
Aluminum	Polished	0.03	0.09
	Anodized	0.84	0.14
	Foil	0.05	0.15
Brick	Red (Purdue)	0.93	0.63
Concrete		0.88	0.60
Earth	Plowed field		0.75
Galvanized sheet metal	Clean, new	0.13	0.65
	Oxidized, weathered	0.28	0.80
Glass, window		0.92	
Ice	Smooth	0.97	
Paints	Black (Parsons)	0.98	0.98
	White, acrylic	0.90	0.26
	White, zinc oxide	0.93	0.16
Paper	White	0.95	0.28
Sandstone		0.85	
Snow	Fine particles, fresh	0.82	0.13
	Ice granules	0.89	0.33
Soot, coal		0.95	
Water	Deep	0.96	
Wood	Sawdust	0.75	
	Oak, planed	0.90	

[a] For a temperature of roughly 300 K.

Radiant exchange between extended parallel plates. Here, we will derive the relation for the case of two extended gray surfaces facing each other in such a way that all the radiation originating from one of the bodies is intercepted by the other (Fig. 7.21). This geometry is found, for example, in flat-plate solar collectors. The two plates will be distinguished by indices 1 and 2. Their radiative properties will be expressed using the emissivities (absorptivities), and the reflectivities. The derivation is of use not only for its result but for the concepts and procedures as well.

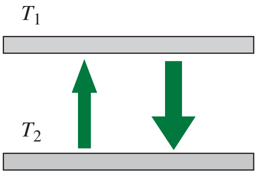


Figure 7.21: Radiant heat exchange between two extended parallel plates. If their temperatures are different, there will be a net flux of energy and entropy from the hotter to the cooler of the plates. (Energy flows are shown here.)

In the course of the derivation, we will need an expression for the total flux of energy per unit area emanating from each of the plates. Since the plates have gray surfaces, they will not absorb all the radiation falling upon them; rather, part of the radiation will be reflected. It is common to call the total flux per unit area, i.e., the *sum of what is emitted and what is reflected*, the *radiosity* $\mathcal{B}$ of the surface. For the plates, the radiosities are

$$\begin{aligned}\mathcal{B}_1 &= e_1\sigma T_1^4 + \rho_1\mathcal{G}_1\\ \mathcal{B}_2 &= e_2\sigma T_2^4 + \rho_2\mathcal{G}_2\end{aligned} \tag{7.60}$$

The reflectivities are related to the absorptivities (emissivities) of a surface, and the irradiance of one of the plates is the radiosity of the other. Therefore,

$$\begin{aligned}\mathcal{B}_1 &= e_1\sigma T_1^4 + (1-e_1)\mathcal{B}_2\\ \mathcal{B}_2 &= e_2\sigma T_2^4 + (1-e_2)\mathcal{B}_1\end{aligned}$$

If we insert the radiosities expressed by Equ.(7.60) into this result, we obtain the following relations for the radiosities of the parallel plates:

$$\begin{aligned}\mathcal{B}_1 &= e_1\sigma T_1^4 + (1-e_1)\left(e_2\sigma T_2^4 + \rho_2\mathcal{G}_2\right)\\ \mathcal{B}_2 &= e_2\sigma T_2^4 + (1-e_2)\left(e_1\sigma T_1^4 + \rho_1\mathcal{G}_1\right)\end{aligned}$$

Now, the net flux density of energy radiated from plate 1 to plate 2 is the difference of the radiosities:

$$\mathcal{B}_1 - \mathcal{B}_2 = e_1e_2\sigma T_1^4 - e_1e_2\sigma T_2^4 + (1-e_1)(1-e_2)(\mathcal{G}_2 - \mathcal{G}_1)$$

Since $\mathcal{B}_1 - \mathcal{B}_2 = \mathcal{G}_2 - \mathcal{G}_1$, this is equivalent to

$$(\mathcal{B}_1 - \mathcal{B}_2)\left[1-(1-e_1)(1-e_2)\right] = e_1e_2\sigma\left(T_1^4 - T_2^4\right)$$

A little algebra finally yields the expression for the net energy flux flowing from the hotter to the cooler of the two parallel plates:

$$I_{E,rad,net} = \frac{\sigma A\left(T_1^4 - T_2^4\right)}{\dfrac{1}{e_1} + \dfrac{1}{e_2} - 1} \tag{7.61}$$

For blackbody surfaces, the emissivities are equal to 1 and we regain the simpler expression already derived in Equ.(7.38).

7.4.5 The Heat Loss Coefficient for Flat-Plate Solar Collectors

Solar collectors provide a very nice application of the kind of heat transfer we have discussed so far. Basically, all three modes of transport take place in the process, which leads to loss of heat from a collector to the surroundings, with radiation and convection at interfaces being the most important.

Solar collectors receive radiation from the Sun; they lose heat to the surroundings when heated above the level of ambient temperature; and they remove heat via fluid flow through the device (Fig. 7.22). Here, we will consider the problem of calculating heat loss. Removal of heat will be dealt with in Chapter 8, while details of the absorption of radiation will be the subject of Chapter 16.

To define the problem of the exchange of entropy and energy with the surroundings, take a closer look at Fig. 7.22. A typical collector consists of an absorber for solar radiation, a duct for the fluid below the absorber which is insulated at the back, and possibly one or two glass covers to reduce top heat loss. The latter process will be the subject of interest in this section. Naturally, heat may also be lost to the back and to the sides, but these effects will not be considered here.

Assume a collector having a single cover made of a sheet of glass. Heat loss from the absorber plate to the environment is the result of the combined effects of radiation and convection from the plate to the cover and from the cover to the air surrounding the collector. Radiation and convection act as parallel modes of transfer from one body to the next, while the transports from the absorber to the cover, and from the cover to the surroundings are in series. Therefore, the combined effect of all modes of transfer can be described by the simple equivalent circuit also shown in Fig. 7.22.

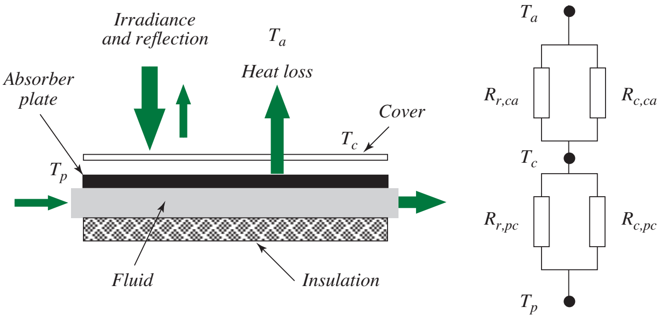


Figure 7.22: Heat loss of a solar collector occurs mostly through the top. The entropy and energy not carried away by the fluid will be transferred to the surroundings. The network on the right symbolizes the combined effect of radiation and convection from the absorber plate to the cover (here it is a single sheet of glass), and from the cover to the surroundings. Subscripts *p*, *c*, and *a* denote the absorber plate, the cover, and the ambient air, respectively, while *r* and *c* stand for radiation and convection.

If we use heat transfer coefficients *h* instead of resistances *R* to calculate the total energy flux due to loss, we can write

$$I_{E,loss} = A_c U_t \left(T_p - T_a\right) \tag{7.62}$$

where

$$\frac{1}{U_t} = \frac{1}{h_{pc}} + \frac{1}{h_{ca}} = \frac{1}{h_{r,pc} + h_{c,pc}} + \frac{1}{h_{r,ca} + h_{c,ca}} \tag{7.63}$$

A_c is the net surface area of the collector (essentially the surface area of the absorber), and U_t symbolizes the total heat transfer coefficient for top loss. Note that conductive transport through the thin glass cover has been neglected in this analysis. If we wish to compute the heat loss coefficient, we have to be able to quantify the heat transfer coefficients for convection and for radiation. While the former pose a problem which we cannot solve at this point,[3] the latter can be expressed in terms of what we have learned so far.

The radiative heat transfer coefficient from the absorber to the cover can be written in the form which will be derived in Example 7.13. If we apply the result derived for radiation between two parallel plates, Equ.(7.61), we obtain

$$h_{r,pc} = \frac{\sigma\left(T_p^2 + T_c^2\right)\left(T_p + T_c\right)}{1/e_1 + 1/e_2 - 1} \tag{7.64}$$

Obviously, in order to calculate this heat transfer coefficient, we need to know the temperatures of both the absorber and the cover. While the former has to be specified, the latter must be obtained as part of the solution of the problem. Now we still need the radiative transfer coefficient for transport from the cover to the surroundings. Radiation occurs between the cover, which has a particular emittance, and the sky for which we use an equivalent blackbody temperature[4] T_{sky}. Therefore, the coefficient turns out to be

$$h_{r,ca} = \sigma e_c\left(T_c^2 + T_{sky}^2\right)\left(T_c + T_{sky}\right) \tag{7.65}$$

See Equ.(7.59). The temperatures strongly depend upon operating conditions, while the convective heat transfer coefficient from the cover to the ambient air is a function of wind speed. Typical values for heat loss coefficients of collectors of the type described are around 5 W/(K · m^2).

7.4.6 Selective Absorbers and Emitters

According to Kirchhoff's law, the emissivity of a surface equals its absorptivity (Section 7.4.4). So why are there two numbers in Table 7.3 for a material, one for its emissivity and one for its absorptivity for solar radiation?

At first sight, Kirchhoff's law seems to pose a riddle. If emissivities equal absorptivities, an application of the laws of radiative heat transfer seem to indicate that bodies should have the same steady-state temperature irrespective of their emissivity/absorptivity. If they are better absorbers of solar radiation, they are better emitters of their own radiation which leads to the same result in balance. However, we know that this is not the case. Different bodies attain different temperatures in Sunlight, the most famous case being our planet whose radiative properties seem to be changing as a result of human activity which is assumed to change the Earth's temperature. Simpler and clearer cases are known from everyday life. Black surfaces get hot faster than shiny white ones when exposed to the Sun.

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[3] We simply have to assume reasonable convective heat transfer coefficients for both transfer from the cover to the surrounding air, and from the absorber to the cover. See Duffie and Beckman (1991; p. 160–176) for a detailed discussion of the problem.

[4] See Duffie and Beckman (1991), p. 158.

The reason is simple: Kirchhoff's law applies, but it applies separately for different types of radiation (see Chapter 14; a and e are equal, but their values change with the wavelength or frequency of the light).

At this point, we shall consider a simple case and apply a steady-state energy balance to find the temperature of a body exposed to sunlight. Take a body completely surrounded by air. The air acts as a black body environment which means that the radiative interaction of body and air lead to a flux of energy of the form of Equ.(7.59). There is an additional interaction because of sunlight. If A_s is the surface area effectively exposed to the Sun, and if $\mathcal{G}_s$ and a_s are the irradiance of solar light and the absorptivity of the surface with respect to sunlight, the rate of absorption will be

$$\Sigma_{E,abs} = a_s A_s \mathcal{G}_s \tag{7.66}$$

If we also allow for convection between the body and the air, the balance of energy in steady-state takes the form

$$a_s A_s \mathcal{G}_s = eA\sigma\left(T^4 - T_{air}^4\right) + Ah\left(T - T_{air}\right) \tag{7.67}$$

Disregard convection for the moment. It is clear that since a_s and e are not equal in general, the steady-state temperature T of the body will depend upon the ratio of emissivity to solar absorptivity. Take a perfect black body ($a = e = 1$ for all wavelengths) or bodies where $a_s = e$ as reference. A body with $a_s / e > 1$ should be warmer than the reference whereas it should be cooler if $a_s / e < 1$.

7.4.7 The Dynamics of an Incandescent Bulb

Here is a nice little application of a dynamical system involving radiation. A small light bulb is connected to a power supply whose voltage is quickly increases from zero and then reduced back to zero equally fast. Voltage across and electric current through the bulb are measured as functions of time (Fig. 7.23, left). If the data is plotted in a current-voltage diagram, we obtain an interesting dynamical characteristic of the bulb (mostly of its tungsten filament; Fig. 7.23, right) which is rather different from the typical steady-state characteristic curves of incandescent bulbs.

Actually, the last leg of the odd shaped characteristic line (part (2) in Fig. 7.23, right) is close to the steady-state characteristic curve; it is the first part that deviates from expectations. The reason for this is simply the drastic changes of temperature of the filament (and other parts of the bulb) as a result of increasing and decreasing dissipation of the energy released in the electric process and the radiating away of the entropy of the hot wire. For the first part of the process, the wire is still cold which leaves the resistivity of the material at a low value. Therefore, the electric current increases faster than in standard experiments where the voltage is raised very slowly step by step. After the peak of dissipation, the wire is hot and the characteristic follows more closely what we know from simple steady-state experiments.

A strongly simplified model of the phenomenon is shown in Fig. 7.24 (left). At its center, it uses the balance of entropy of the tungsten wire in the bulb. There are two main processes taking place: entropy is produced in the wire and is radiated away. The entropy of the body defines its temperature which, in turn, is used to express the constitutive laws for the production rate and the source rate of entropy. Details of the model concern the resistivity and the emissivity of tungsten which are functions of temperature (the temperature dependence of the entropy capacitance has not been included).

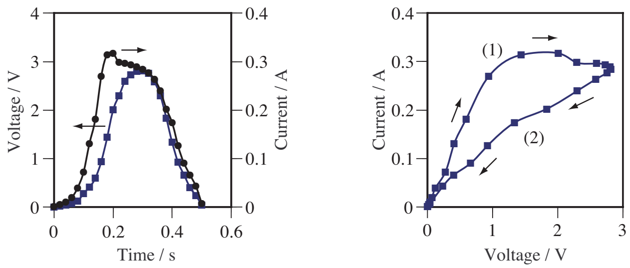

Figure 7.23: Data of voltage and electric current for a small incandescent bulb that is quickly turned on and off, as functions of time (left) and in the form of the current-voltage characteristic (right).

The law of balance of entropy for the tungsten wire includes the production rate due to dissipation of energy and a source rate as a result of radiation:

$$\dot{S} = \Pi_S + \Sigma_{S,rad} \tag{7.68}$$

We need three constitutive laws to complete the model: one for the temperature-entropy relation of a body made of tungsten (Section 4.5), one for the production rate of entropy (Section 4.4.2), and the last for the radiation of entropy by the hot wire. Fundamentally, each of the relations includes a temperature dependent material property, namely, specific entropy capacitance in the first case, electric resistivity in the second, and emissivity in the third.

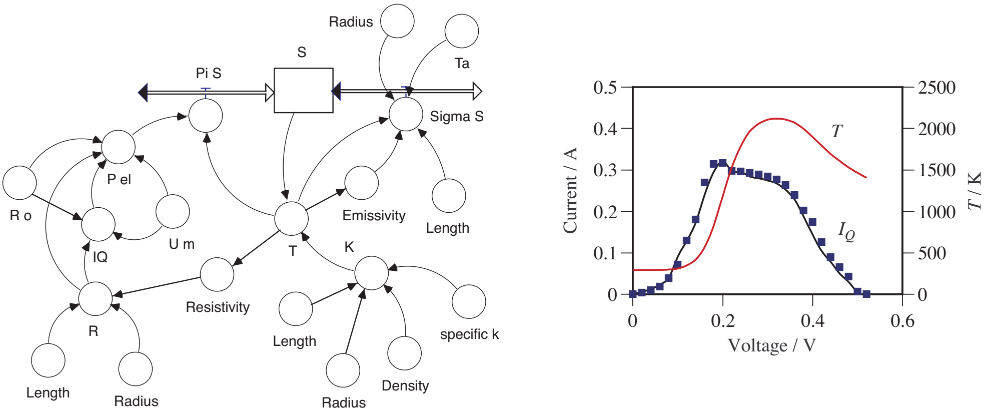

Figure 7.24: Diagram of a simple dynamical model of the tungsten wire (left) and data (squares) and simulation results for the electric current through the wire and the temperature of the wire (right).

In the present model, I have chosen not to include the temperature dependence of the entropy capacitance. Rather, an average value of κ has been estimated as follows. The specific heat of tungsten varies between 130 J/(K·kg) and 180 J/(K·kg) in the expected range of temperatures (300 K to 3000 K). We can divide an average value of the specific heat by an average value of the temperature to obtain a first approximation to the entropy capacitance:

$$K_{av} = m\left(c/T\right)_{av} \tag{7.69}$$

The mass m of the wire is obtained from the density and the volume where the latter is calculated from the length and radius of a cylindrical body (the radius will turn out to be a critical unknown parameter of the model). With a constant entropy capacitance, the entropy temperature relation is simply

$$S = K_{av}T \tag{7.70}$$

Now we need an expression for the entropy production rate in the tungsten wire. The first step is simple: the production rate equals the electric dissipation rate divided by the temperature of the wire. The latter is obtained from the entropy, Equ.(7.70), and the former equals the voltage times the electric current. The voltage across the wire is a part of the measured voltage U_m that will be used as an input to the model (see the model diagram in Fig. 7.24). It represents only a part of U_m since there are connecting elements (copper connectors) to the tungsten filament inside the bulb. They will be given a constant (unknown) resistance R_0, another simplification in our model:

$$U_T = \frac{R}{R+R_0}U_m$$

where R and U_T are the resistance of and the voltage across the filament, respectively. The electric current through the bulb will be

$$I_Q = \frac{1}{R+R_0}U_m$$

so the entropy production rate turns out to be equal to

$$\Pi_S = \frac{1}{T}\frac{R}{\left(R+R_0\right)^2}U_m^2 \tag{7.71}$$

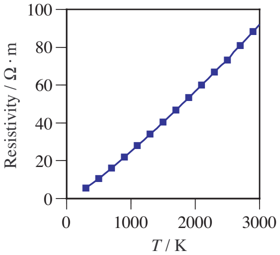

Figure 7.25: Electric resistivity of tungsten, as a function of temperature.

The second important material property of the filament concerns its resistance or rather, its *resistivity*. It can be introduced as an interpolation function of data in Fig. 7.25. The resistance of the wire is

$$R = \rho_{el}\frac{l}{\pi r^2} \tag{7.72}$$

Finally, the rate of emission of entropy from the tungsten wire must be found. The source rate of entropy equals the source rate of energy divided by the temperature (Equ.(7.44)). The energy source rate equals the energy flow which can be obtained from Equ.(7.59):

$$\Sigma_S = \frac{1}{T}aA\sigma\left(T^4 - T_a^4\right) \tag{7.73}$$

The absorptivity a equals the emissivity which is obtained from data as in Fig. 7.20.

This pretty much concludes the dynamical model. It can be used to predict the electric current through the bulb which can be compared to measurements (see the diagram on the right in Fig. 7.24). In addition, the model yields results on the temperature of the filament. This confirms the initial idea about why the bulb behaves in the manner observed. The temperature of the wire rises slowly at first and then stays high beyond the point in time where the lamp is turned off again.

The good agreement between simulation and measurements should not be taken as a sign of the model's perfection. It suffers from several shortcomings, but clearly it gives an understanding of the most basic phenomena. Structurally, we have left out at least a couple of important elements. For one, the thermal and electric dynamics of the connecting (copper) elements should be included in the model similarly to how this was done for the filament. Secondly, the entropy radiated from the filament is intercepted at least partly by the glass of the bulb; we might want to include the glass as an additional element in our model. Then, as mentioned before, the entropy capacitance should not be taken as constant—the range of temperatures is too great. Moreover, to get a halfway reliable model we should measure the geometric properties of the filament and connecting wires as carefully as possible.

QUESTIONS

16. Why is the measure of the flow of entropy through the radiation field not a standard current? Why is the measure of the rate of emission from a body to a field (or vice-versa) a source rate and not a current?
17. Why does the basic relation $I_E = TI_S$ not apply to radiation flowing through the radiation field? Does the analogous relation hold for sources and sinks of energy and entropy in radiative interaction between bodies and fields?
18. What simple argument shows that emission of radiation is dissipative?
19. Sunlight, i.e., the light flowing through the radiation field from Sun to Earth, has a temperature of nearly 6000 K. The light radiated by our planet has a temperature close to 300 K. What is the ratio of the entropy per unit energy for these two types of radiation?
20. If, on balance, the Earth radiates away as much energy as it receives from the Sun, how much entropy is produced by the planet?
21. Consider an imaginary sphere having a large radius (such as the distance from Sun to Earth) drawn around the Sun and consider one square meter of this surface through which the Sun's light is flowing. Are the values of $\mathcal{E}$ and $\mathcal{E}_S$ the same as at the surface of the Sun?
22. Consider the opaque surface of a warm body surrounded by air. There is radiation alongside convective entropy transfer. Are the processes in parallel or in series?
23. Imagine a spherical rock in space (a planet without atmosphere) exposed to the light of the Sun. In steady-state it will attain a certain temperature. Does this temperature depend upon the emissivity of its surface?
24. Does galvanized sheet metal get hotter in sunlight than a surface painted black?

EXAMPLE 7.11. Surface temperature of the Sun.

The radiation originating in the thin surface layer of the Sun has properties almost like those of a black body. (a) Using the solar constant (1370 $\mathrm{W/m^2}$), the distance from the Earth to the Sun ($1.5 \cdot 10^8$ km), and the Sun's radius (700,000 km), derive the temperature of its surface. (b) Calculate the rate at which entropy is emitted by the total surface.

SOLUTION: (a) The solar constant $\mathcal{G}_{sc}$ is the value of the energy flux per unit normal area at the distance of the Earth. Using this value we calculate the emissive power of the Sun (called the luminosity L):

$$L = 4\pi d^2 \mathcal{G}_{sc} = 4\pi \cdot \left(1.5 \cdot 10^{11}\,\text{m}\right)^2 \cdot 1370\,\text{W}/\text{m}^2 = 3.9 \cdot 10^{26}\,\text{W}$$

The Sun approximates a black body which does not receive radiation from the surrounding space. Therefore, Equ.(7.36) applies to the relation between emissive power and temperature, leading to a value of

$$T = \left(\frac{L}{4\pi R_{sun}^2 \sigma}\right)^{1/4} = \left(\frac{3.9 \cdot 10^{26}\,\text{W}}{4\pi \cdot \left(7.0 \cdot 10^8\,\text{m}\right)^2 \cdot \sigma}\right)^{1/4} = 5770\,\text{K}$$

for the surface temperature of the Sun.

(b) The entropy flux flowing away from the Sun through the field is given by

$$I_S = \frac{4}{3} A \sigma T_{sun}^3 = 8.95 \cdot 10^{22}\,\text{W}/\text{K}$$

EXAMPLE 7.12. Surface temperature of the Earth.

Model the Earth as (a) a black body of uniform temperature, absorbing radiation from the Sun and emitting radiation to outer space. How large is the value of the temperature attained by the surface of this body in steady state? (b) Repeat this for a gray surface and again (c) for a black radiator that absorbs 70% of sunlight (because of reflection by snow and clouds).

SOLUTION: (a) We can use Equ.(7.67) without convection and $T = 0$ K for the environment. This yields

$$A_s \mathcal{G}_{sc} = A \sigma T^4$$

A_s is the projected surface of a the sphere (a circle) and A is the surface of the planet. Inserting and solving for T leads to

$$T = \left(\frac{\mathcal{G}_{sc}}{4\sigma}\right)^{1/4} = \left(\frac{1370\,\text{W}/\text{m}^2}{4\sigma}\right)^{1/4} = 279\,\text{K}$$

(b) For non-black bodies we have

$$a_s A_s \mathcal{G}_{sc} = e A \sigma T^4$$

Since $a_s = e$ for gray surfaces, the new condition leads to the same result for the temperature of the planet, $T = 279$ K.

(c) If the Earth radiates like a black body, $e = 1$. However, if it reflects 30% of incoming radiation, we may set $a_s = 0.7$ (it is as if the planet were a selective absorber/radiator). Now we have

$$T = \left(\frac{a_s \mathcal{G}_{sc}}{4 e \sigma}\right)^{1/4} = \left(\frac{0.7 \cdot 1370\,\text{W}/\text{m}^2}{4\sigma}\right)^{1/4} = 255\,\text{K}$$

All three results are too low. The mean surface temperature of our planet is more like 288 K, leaving us with the problem of how to explain this difference (see Chapter 9, Section 9.6).

EXAMPLE 7.13. The radiative heat transfer coefficient.

Write the equation for the exchange of energy between a black body and its surroundings, Equ.(7.38), in a form which resembles the equation of convective heat transfer at a solid–fluid boundary. How would you write the overall heat transfer coefficient, including convection?

SOLUTION: It is possible to transform the term involving the difference of the fourth powers of the temperatures in such a way that the difference of temperatures occurs in the equation:

$$\begin{aligned} I_{E,rad,net} &= \sigma A\left[T_1^4 - T_2^4\right] \\ &= \sigma A\left(T_1^2 + T_2^2\right)\left(T_1^2 - T_2^2\right) \\ &= \sigma A\left(T_1^2 + T_2^2\right)\left(T_1 + T_2\right)\left(T_1 - T_2\right) \end{aligned}$$

Comparison with the desired form, Equ.(7.27), shows that

$$h_{rad} = \sigma\left(T_1^2 + T_2^2\right)\left(T_1 + T_2\right)$$

Obviously, the radiative heat transfer coefficient strongly depends upon the temperatures involved.

If convection is present as well, we are dealing with a case of parallel flow of heat. The flux of energy is equal to the sum of the radiative and the convective fluxes. Therefore, the overall heat transfer coefficient must be equal to the sum of the radiative and convective transfer coefficients.

EXAMPLE 7.14. Absorption of solar radiation: the balance of entropy.

A body absorbs a fraction *f* of the energy current associated with solar radiation I_E intercepted by it. Represent the losses to the environment in terms of a total heat transfer coefficient *h* (which includes radiation). Assume that solar radiation does not carry any entropy. (Because of the high temperature associated with solar radiation, this assumption is quite applicable here.) (a) Calculate the sum of the rates of entropy generation due to absorption of radiation and losses. (b) Show that you obtain the same result using the balance of entropy for the body if you take the system boundary to coincide with the environment at temperature T_a. (c) Compare the magnitude of the effects for a body with a surface area of 1.0 m^2 at a temperature of 50°C absorbing 80% of an energy flux of 1000 W/m^2 in an environment of 20°C. The heat transfer coefficient has a value of 10 W/(K·m^2).

SOLUTION: For the solution of the problem we will need the equation of balance of energy for the body:

$$\dot{E} = \Sigma_E - I_{E,loss} = f I_E - hA\left(T - T_a\right)$$

(a) Entropy production is due to two distinct irreversible processes, the absorption of radiation and heat transfer to a colder body (the environment). Since the energy of solar radiation absorbed is dissipated, the rate of production due to absorption of radiation is

$$\Pi_{S1} = \Sigma_E / T$$

The rate of production of entropy as a result of heat transfer, on the other hand, is given by

$$\Pi_{S2} = hA\left(T - T_a\right)\left(\frac{1}{T_a} - \frac{1}{T}\right)$$

(b) If we consider the body as our system and draw the system boundary at the location of the environment at temperature T_a, we include the part responsible for heat transfer in the system. In this case, the equation of balance of entropy takes the form

$$\dot{S} = I_S + \Pi_S$$

Remember that the radiation is assumed not to deliver any entropy, so there is no source term. Now we have

$$\Pi_S = \frac{\dot{E}}{T} - \frac{I_{E,loss}}{T_a} = \frac{f I_E - hA(T - T_a)}{T} + \frac{hA(T - T_a)}{T_a}$$

This result is equivalent to what we obtained by calculating the rates of production independently.

(c) Inserting the numbers into the expression obtained in (a) gives values of 2.5 W/K and 0.095 W/K, respectively. This tells us something about the relative irreversibilities of the processes (absorption and heat loss): the former is much larger. If we wanted to optimize a system by minimizing entropy production, we have to be able to quantify different contributions to irreversibility (see Chapter 9 for a discussion of this approach).

EXERCISES AND PROBLEMS

1. Sunlight passes in one direction through a gas inside a long cylinder. The flux of entropy at the surface where the light is entering has a magnitude of 5.0 W/K. At the opposite end, the flux of the current of entropy leaving the body is 4.0 W/K. (a) Determine the net flux of entropy with respect to the region of space occupied by the body. (b) At what (minimal) rate is the entropy of the body changing? (c) What is the value of the source rate of entropy for the field? How large is the flux of entropy with respect to the material body?
2. A copper bar of length 0.50 m and cross section 10.0 cm^2 has a temperature of 500 K at one end and 300 K at the other. As heat flows through the bar in steady state, measurements indicate that the temperature varies linearly along the bar. (a) Determine the temperature gradient. Take the direction of entropy flow to be positive. (b) Estimate the current densities of entropy and of energy for the center of the bar using the values read from Fig. 7.8. How large is the conductivity with respect to energy? (c) Divide the bar into two equal parts. With this current of entropy flowing, what is the flux of entropy at the surface where the parts touch with respect to the part from where the entropy is flowing?
3. An immersion heater in a water kettle is hooked up to 220 V. Its electrical resistance is 160 Ω at a temperature of 20°C; the temperature coefficient of the resistance is $4 \cdot 100^{-3}$ K^{-1}. If the heat transfer coefficient between heater and water is 100 $W/(K \cdot m^2)$ and the surface area of the heater is 0.020 m^2, how large will the energy current from the heater to the water be? How does the situation change if a layer of mineral deposit builds up around the heater?
4. Show that the energy current transmitted through a cylindrical shell of length L having inner and outer radii r_1 and r_2 is

$$I_E = \pi L \left[\frac{1}{2r_1 h_1} + \frac{1}{2r_2 h_2} + \frac{1}{2k_E} \ln\left(\frac{r_2}{r_1}\right) \right]^{-1} (T_1 - T_2)$$

   where h_1 and h_2 are the inner and the outer convective heat transfer coefficients. The temperatures of the fluids on the inside and the outside are T_1 and T_2.
5. A cylindrical volume of rock below ground has been heated uniformly to 50°C while the rest of the rock has a temperature of 10°C. (This might be done in solar seasonal heat storage applications.) Use the average values for granite for the properties of the rock. (a) Make

the following model for heat loss from the cylindrical area to the surroundings. While the temperatures of the storage area and the surroundings remain uniform, heat flows through a cylindrical mantle with inner and outer radii equal to half and to twice the radius of the storage cylinder, respectively. Estimate the energy current due to heat loss for a radius of 5.0 m and a length of the cylindrical space of 40 m. (b) How large should the radius be made for heat loss over a period of half a year not to exceed one quarter of the energy stored in the cylinder?

6. A sheet of metal with a selective surface of 2.0 m^2 lies horizontally on the ground. The bottom of the sheet is well insulated. In the visible part of the spectrum the emission coefficient of the metal is 0.90, while in the infrared it is 0.30. Take the ambient temperature to be 20°C. The Sun stands 50° above the horizon, and 70% of the radiation outside the atmosphere penetrates the air. (Assume all the radiation from the sky to be direct and not diffuse.) (a) Neglecting convection, how large should the temperature of the metal sheet be in the light of the Sun? (b) Now take into consideration convective heat transfer at the upper surface of the sheet. The convective heat transfer coefficient is assumed to be 14 W/($K \cdot m^2$). Calculate the temperature attained by the sheet under these conditions.

7. Hot water is left to cool in a thin-walled aluminum can. In a first experiment, the aluminum is highly polished (curve number 1 in Fig. P.7). In the second experiment (curve 2), the can is painted black. Assume the convective transfer from the water to the can to be highly efficient. Data: Mass of water: 0.476 kg; surface area of the can: 0.0325 m^2; Ambient temperature: 21.6°C. (a) Determine the rate of change of entropy of the water in Experiment 1 at $t = 500$ s? (b) Assume radiation to be negligible in Experiment 1. What are the convective entropy and energy transfer coefficients for the surface of the can (can to air). (c) Use the data of Experiment 2 to determine the emissivity of the black surface.

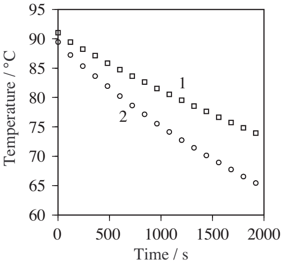

Figure P.7

8. Normally, the surface temperatures of stars are derived from their colors or their spectra. However, it is also possible to calculate this quantity from the intensity of their light (i.e., from the irradiance at the surface of the Earth), and from their angular diameter as seen from the Earth. Angular diameters of some nearby stars can be determined with the aid of interferometric methods. In the case of the star Sirius in the constellation of Canis Majoris, these values are $8.6 \cdot 10^{-8}$ W/m^2, and $6.12 \cdot 10^{-3}$ arc seconds, respectively.

9. Consider the Earth as a uniform body. (a) How large is the rate at which entropy appears in the atmosphere, biosphere, and the oceans of the Earth if we take their temperature to be 300 K? The solar constant outside the atmosphere is 1.36 kW/m^2. 30% of the radiation is directly reflected back into space. (b) How large is the flux of entropy through the radiation field just before radiation is absorbed? (c) How large is the rate of production of entropy on the planet as a result of absorption? (d) How large is the rate of entropy generation overall?

10. A photovoltaic panel with an area of 1.0 m^2 is exposed to constant solar radiation having an energy current of 800 W/m^2. Initially, panel and cells are at ambient temperature (300 K). The panel has a heat capacity (energy capacity) of 1000 J/K. The absorption coefficient of the panel for sunlight is 0.85. The emission coefficient of the panel for thermal radiation is 1. Energy goes directly to the air as well (the heat transfer coefficient is 12 W/($K \cdot m^2$)). The electric efficiency of the panel decreases with temperature according to

$$\eta = 0.15 - b\left(T - T_a\right) \quad , \quad b = 1.667 \cdot 10^{-3}\,\mathrm{K}^{-1}$$

The efficiency is defined as the ratio of electric power and energy current of sunlight (not the absorption rate!). (a) What is the electric power right at the beginning? (b) Formulate the law of balance of energy of the panel in general (instantaneous) form. (c) What is the rate of change of temperature of the panel right at the beginning? (d) Determine the steady-state temperature of the panel resulting after a period of time. (e) Sketch as precisely as possible, the temperature and the electric power of the panel as functions of time.

11. A spherical satellite with a radius of 0.50 m moves in a low orbit around the Earth (Fig. P.11.1). Approximately half the time it is exposed to the Sun's light (the solar constant is

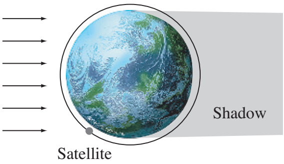

Figure P.11.1

1370 W/m^2). In the Earth's shadow it is irradiated by the earth itself. The satellite is a thin aluminum shell. (a) The Earth absorbs approximately 70% of the energy of the incident light of the Sun. The energy is then uniformly reradiated over the entire surface. What is the energy flow of the earth's radiation per square meter? (b) Calculate the highest and the lowest steady-state temperatures reached by the satellite. This temperature is uniform over the entire surface. Assume that the satellite is a black body radiator. When it is in sunlight, ignore the Earth's radiation. (c) Determine the mass of the satellite with the help of the temperature as a function of time (see Fig. P.11.2).

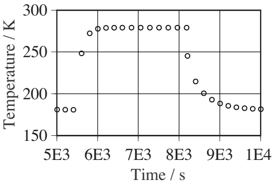

Figure P.11.2

12. In solar energy applications, parabolic troughs are used to focus light upon absorbers of cylindrical shape. Calculate the heat loss coefficient of such an absorber. Consider it to be made of a metal pipe having a diameter of 5.5 cm, surrounded by a thin glass cover with an outer diameter of 8.5 cm. The annulus between the pipe and the cover is evacuated. Take the convective heat transfer coefficient at the surface of the cover to be 35 W/(K·m^2). The emissivities of glass and the metal pipe are 0.88 and 0.92, respectively. Present the result as a function of absorber temperature for an ambient temperature of 20°C.

13. A bottle of white wine is placed in a refrigerator whose inner temperature we take to be constant at 0°C. How long will it take for the temperature of the wine to decrease from an initial value of 20°C to the desired 8°C? Treat the wine as a uniform system of mass 0.75 kg and use the constitutive quantities of water. The bottle is made out of glass with a thickness of 5.0 mm. The height and the diameter of the main body of the bottle are 25 cm and 8 cm, respectively; neglect its bottom and its neck and treat the mantle as a flat layer. The convective transfer coefficients inside and outside are 200 W/(K·m^2) and 10 W/(K·m^2), respectively.

14. A spherical thin-walled water tank has a volume of 1.0 m^3. The water inside is kept at a constant temperature of 60°C by heating it with an energy current equal to 1.0 kW. The ambient temperature is 15°C. How long will it take for the water to reach a temperature of 40°C after the heater has been turned off?

15. A body of water having a volume of 1.0 m^3 loses heat to its surroundings. The temperatures are 80°C and 20°C for the water (initially) and the environment, respectively. The product of total heat transfer coefficient and surface area is 60 W/K. (a) How long does it take for the temperature difference between the water and the surroundings to decrease to half its initial value? (b) How large is the rate of production of entropy right at the beginning? (c) How much entropy is produced in total from the beginning until the water has cooled down completely? (d) How much energy could have been released by an ideal Carnot engine operating between the water and the environment as the water cools to ambient temperature?

16. To maintain an inner temperature of 20°C in a building situated in a 0°C environment, the required heating load is 5 kW. Without heating, the house is found to cool down as follows: every day, its temperature decreases by 1/5 of the temperature difference to the environment. (a) Determine the product of surface area and total heat transfer coefficient. (b) Model the building as a single node system. Calculate its temperature coefficient of energy. (c) Assume the temperature inside the building to be 12°C. Calculate the heating power necessary if you wish the temperature to rise by 1°C per hour.

17. A tall, well insulated cylinder of radius 0.75 m contains 10,000 kg of water. The lower 3500 kg has a temperature of 20°C, while the temperature of the rest of the water is 80°C. Such stratification may be approximately attained while charging a hot water storage tank in solar applications. (a) Estimate how long it will take for the difference of the temperatures of the two segments of water to decrease to 30°C. (*Hint:* Model the segments as uniform bodies; for the thermal resistance take a distance from the center of the hotter to the center of the cooler part.) (b) Calculate the initial rate of production of entropy. (c) How large is the initial rate of loss of available power?

CHAPTER 8

FLOW SYSTEMS AND CONVECTIVE TRANSPORTS

In Chapter 7, we dealt with entropy transfer in *closed systems*. Closed systems do not exchange matter with the environment. In other words, they are non-flow systems. *Flow systems*, on the other hand, allow matter to cross the boundary of a control volume. These are called *open systems*.

As discussed in Section 7.1.2, it is a matter of opinion what a flow system actually is. When air flows in the atmosphere or water in a pipe, we may follow a well defined and identifiable piece of matter. We think of an imaginary boundary around this body and apply the analysis for closed systems presented in Chapters 4, 5 and 7. In many cases, however, it makes more sense to perform an analysis based upon a control volume. This viewpoint is often suggested by some machinery through which a fluid passes. A simple case would be a pipe with water flowing through it. If we define the inside surface of the pipe as the boundary of a control volume, it is penetrated by two currents, one at the entrance and one at the outlet.

Fluids flowing into and out of—or through—some region of space carry with them the fluidlike quantities they contain. Among these quantities are entropy, dissolved substances, momentum and, indirectly, energy.[1] In this chapter, the currents of these quantities carried by a fluid will be considered; such currents are called *convective*.

Flow systems abound in nature and in machines. In a study of open systems, the number of possible applications literally explodes. To prepare for interesting and important examples, I shall take a brief look at convective transfer of (dissolved) substances and momentum before turning to the flow of entropy. Other parts of the chapter are devoted to a discussion of energy in flow systems; here we extend the notion of chemical potential to fluids in systems that allow for transfer of matter.

8.1 THERMAL PHENOMENA IN FLOW SYSTEMS

To get a feeling for flow systems, let us study a couple of simple small-scale examples and introduce brief word models. The first is an experiment where hot water from a tin can flows into a can containing cold water; the second container has an outflow. In

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[1] Energy flows are different from flows of the other quantities which underlines its special nature once again.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_9,

the second example, water in an open glass container is heated electrically and vaporized. After some time, the heater is turned off and the water is left to cool.

Mixing hot and cold water in a flow system. Two small tin cans, each with an outlet, contain water. Hot water from the first flows into the second from above (see Fig. 8.1, left). Originally, there is only a small amount of cold water in the second can (see water levels in Fig. 8.1, center, temperatures are on the right). Liquids in both containers are stirred continuously.

As the level of water drops in Tank 1, it first rises in Tank 2 and then drops. The temperature of the liquid in the first can drops. In the second tank, the temperature rises and then falls.

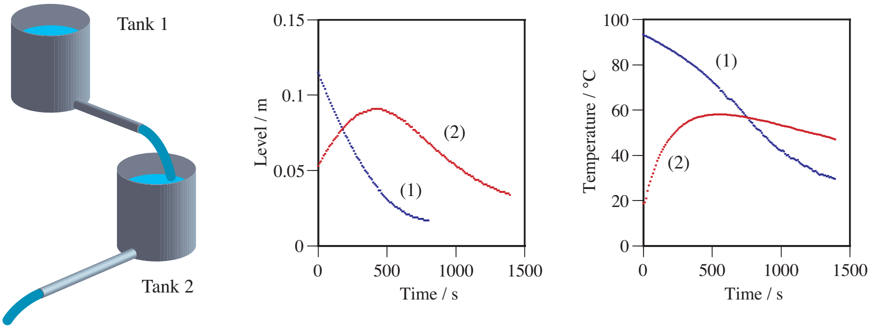

Figure 8.1: Hot water in Tank 1 is let flow into (a small amount of) cold water in Tank 2. Tank 2 has an outlet. The water in both tanks is stirred continuously. Water levels (center) and temperatures (right) are measured in both tanks.

Interpretation. The behavior of the levels of liquid as functions of time is pretty much as expected. Details may be different from a simpler case where fluid temperatures do not change (see examples in Chapter 1). This is so because the temperature determines the viscosity of the water which may critically influence the type of flow.

The more interesting part of the phenomenon is the thermal behavior of the system. Note the drop of temperature in Tank 1. Here we have the usual suspect: heat loss to the environment. We have two types of losses: entropy transfer through the thin wall of the tin can, and cooling due to evaporation. The measured temperature differs from a simple cooling curve: the (negative) rate of change of temperature increases as time goes on. The reason for this unexpected behavior is to be found in the fact that the mass of liquid in the tank decreases rather quickly for the first 400-500 seconds.

The temperature of the water in Tank 2 initially rises since hot water flows in and is mixed with the cold liquid; the water from the first can carries a lot of entropy. T_2 starts to fall even before the water from the first container has become colder than the water present in system 2 (Fig. 8.1, right). The reason for this is entropy loss just as in the case of Tank 1. The shape of T_2 after about 800 s is similar to that of T_1 during the first phase of the experiment, again for the same reason (decrease of the amount of water in the second can).

Heating and evaporating water in an open container. In the second experiment, water is heated electrically inside a glass. The water is stirred, temperature and mass of the water are measured (the assembly stands on a recording scale, see Fig. 8.2, left).

The temperature rises slightly faster at the beginning than later on. When the fluid starts boiling, the temperature remains constant. At 1600 s, the heater is turned off and the water is left to cool.

Continuous measurement of the mass of liquid can be used to determine the mass flux caused by evaporation (Fig. 8.2, right). The flow of steam rises sharply as the water nears the boiling point, stays (roughly) constant during boiling and then drops as soon as the heater is turned off and the temperature decreases.

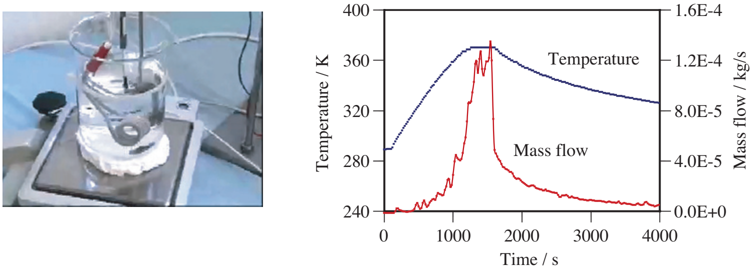

Figure 8.2: Water is heated electrically in an open glass and stirred continuously. The assembly sits on a scale. The heater is turned off after about 1600 s.

Interpretation. The rise of temperature during the first part of heating is a classic behavior. It slows somewhat because of increasing loss: the temperature difference between water and environment increases. Constant temperature during boiling is a well known phenomenon. The final lowering of temperature is clearly due to entropy loss.

So far so good. Data of the current of mass, however, gives us additional information. This transport is due to evaporation: steam leaves the system. Clearly, the flow of matter increases with increasing temperature.

On further thought, cooling by evaporation (which also took place in the first experiment described, Fig. 8.1) needs some additional explaining. It is clear that the water leaving the system removes entropy. Consider the case where someone pours some water out of a tank. This does not change the temperature of the water in the system since the fluid leaving takes the quantity of entropy it contains according to its temperature with it. This leaves the remaining liquid with just the right amount of entropy for its temperature to stay constant. Evaporation by cooling must therefore result from a higher than expected entropy flux with steam. A little more thinking explains what is happening: steam transports the entropy it contains as hot water plus the entropy it obtains when it turns to steam. What we learn is this: *currents of matter transport the entropy contained in them.*

8.2 CONVECTIVE TRANSPORTS AND BALANCES IN OPEN SYSTEMS

The case of convective transfer—meaning the bulk flow of a fluid and the associated transport of entropy, momentum or substances stored in the fluid—is a rather simple concept. The expression for convective currents of fluidlike quantities is always the same. It is understood most easily if we consider dissolved substances in a material such as salt in water carried by the flowing liquid (Section 8.2.1). The notion of dissolved substance will be extended to momentum (Section 8.2.2, see also Chapter 3, Section 3.1.3) and entropy (Section 8.2.3).[2] Energy transfer in flow systems will be introduced subsequently in Section 8.2.4. Here we will encounter once again the special role taken by energy—expressions for flow energy are different from relations for convective currents of substances, entropy, or momentum.

Laws of balance make up the second basic element of flow systems analysis. We have met the generic law of mechanics—the balance of momentum—including convective momentum currents in Section 3.4. We can follow this example when we formulate laws of balance for dissolved substances, entropy, and energy in Section 8.2.5.

8.2.1 Convective Transport of Dissolved Substances

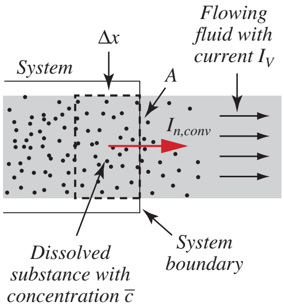

Figure 8.3: A fluid (shaded) carries a dissolved substance (dots) across the boundary of a system.

Consider water flowing across the boundary of a system, as in Fig. 8.3. Salt is dissolved in the liquid and carried along with it. Now imagine a small region just behind the boundary (rectangle with dashed border, Fig. 8.3) where the molar concentration of salt is equal to $\bar{c}$ (Equ.(6.14)). The amount of salt contained in the region, i.e., $\bar{c}A\Delta x$, takes a time Δt to flow out of the system so the current of amount of salt is $I_n = \bar{c}Av$. Since Av equals the current of volume of water, I_V, the convective current of amount of dissolved substance $I_{n,conv}$ is given by

$$I_{n,conv} = \bar{c}I_{V,fluid} \tag{8.1}$$

Common sense suggests that this should be so: the amount of the dissolved substance carried across the system boundary per unit time must be proportional to the current of the carrier substance and to how much stuff is dissolved per unit volume of fluid (density of amount of substance or concentration). Note that $I_{V,fluid}$ is based upon the volume of the solution which may be different from the volume of the solvent alone.

It is quite common to use the flux of mass I_m of the fluid instead of its current of volume. If we use the definition of mass fraction x_s of the solute (Equ.(6.11)), we arrive at the equivalent expression for a convective current of amount of substance:

$$I_{n,conv} = \frac{1}{M_{0,s}} x_s I_{m,fluid} \tag{8.2}$$

The index s refers to the solute, i.e., the dissolved substance, and $I_{m,fluid}$ is the total mass flux, that of solute and solvent.

Equ.(8.1) assumes that the density (concentration) of the dissolved substance is the same over the entire surface through which the fluid flows. If this were not the case, we could replace the expression by a more general one involving the current densities j_n and $j_V = v$:[3]

$$j_{n,conv} = \bar{c}v \tag{8.3}$$

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2. We have already seen a case that is similar in some respects: if the fluid is (thermal) radiation, the entropy transfer can be understood if we imagine entropy “dissolved” in the “substance” called radiation; entropy transfer is calculated with the help of the relation that gives us the entropy stored in radiation (Section 7.4.1, and Chapter 12).
3. Current densities were introduced briefly in Section 7.2.1 (Equ.(7.14)); they will be used intensively in Chapters 11 and 12 and in Part IV.

Naturally, Equ.(8.2) can also be replaced by its local counterpart. Local formulations become important when we discuss spatially variable situations.

Mixing salt and water in a flow system. The simplicity of the concept of convective currents is demonstrated quite easily by an experiment in which fresh and salt water are mixed (Fig. 8.4). Consider the simple hydraulic system made up of two (equal) tanks connected at their bottoms by a pipe. The second tank has an additional outflow. Salt water is filled to a level of 5 cm into the first tank. The second tank initially contains fresh water (to a level of 30 cm). When the water is let flow, it flows out of the second tank into the first and into the environment. As the level of water rises in Tank 1, the concentration of the salt there decreases because fresh water is mixed with the salty liquid (the water in Tank 2 remains fresh). When the levels of liquids in the two containers have become equal (roughly at 120 s, see the graph in Fig. 8.4), the flow in the connecting hose reverses its direction. From now on, salt water enters the second tank and is mixed in with the fresh water. As a result, the concentration of salt in the water of Tank 2 increases.

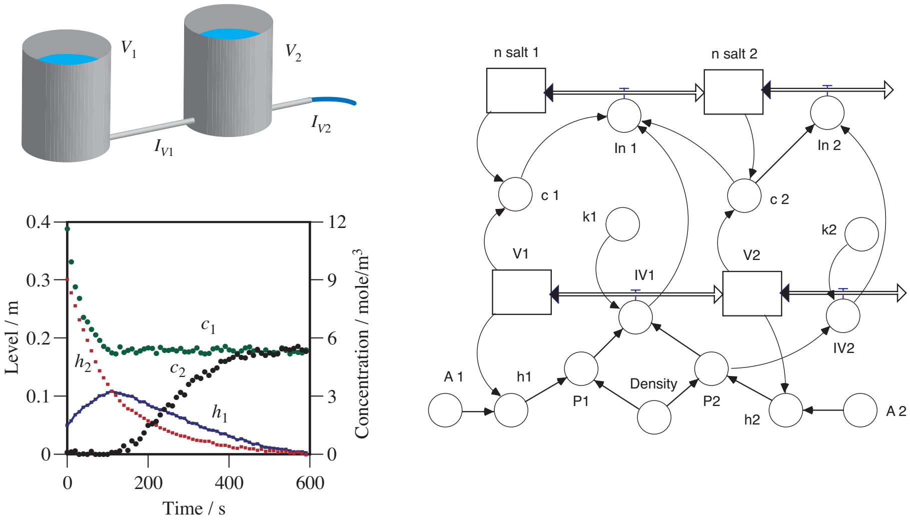

Figure 8.4: Two tanks contain salt water (Tank 1) and fresh water (Tank 2) initially. The tanks are connected by a hose, and there is an outlet from Tank 2 into the environment. The water in the two tanks is continuously stirred. Data of water levels and of salt concentration (measured as conductivity of the liquids) has been taken (diagram on the left). Right: Diagram of a dynamical model of the system.

A dynamical model of the system may take the form of the system dynamics diagram shown on the right in Fig. 8.4. There are four fluidlike quantities to be accounted for: amounts of water in the two tanks, and amounts of salt dissolved in the water in the tanks. We add to this two water flows and two (convective) currents of salt. If we assume the concentration of salt to be small enough for the density of the water not to be affected too strongly, and if we assume the flow properties of the liquids to be those of pure water, the hydraulic part of the model is independent of the chemical properties and is constructed along the lines discussed in Chapter 1. In order to understand the salt concentration of the water in the two tanks, we have to introduce (molar) concentrations of salt into the model and express the convective currents of salt in terms of these concentrations and the volume fluxes of water. The current of salt flowing between the two containers depends upon the concentration in Tank 1 if water flows from there to Tank 2 (which is the case after 120 s). If water flows from Tank 2 to Tank 1 (before 120 s), the convective current depends upon $\bar{c}_2$:

$$\begin{aligned} I_{n,NaCl,1} &= \bar{c}_1 I_{V1} \quad , \quad if\ P_1 > P_2 \\ I_{n,NaCl,1} &= \bar{c}_2 I_{V1} \quad , \quad if\ P_1 < P_2 \end{aligned} \tag{8.4}$$

The current of salt out of Tank 2 into the environment always depends upon the salt concentration in the second container. This simple model yields quite satisfactory results as can be seen from the comparison of simulation results with data (Fig. 8.5).

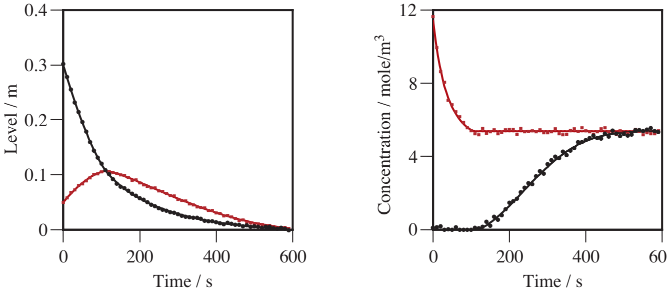

Figure 8.5: Simulation results of model in Fig. 8.4 and experimental data.

8.2.2 Convective Momentum Currents

The example of convective momentum currents was already discussed in Chapter 3 (see Section 3.4, Equ.(3.25)). It makes sense to repeat this to compare the result to what we just had for chemical currents. If we take Equ.(8.1) as a guide we see that a convective momentum current must be equal to the momentum per volume, i.e., the density of momentum, multiplied by the flux of volume of the fluid, i.e., $p/V \cdot I_V$. This can be transformed to yield the product of the momentum per mass of fluid and the mass flux of the fluid:

$$I_{p,conv} = v I_{m,fluid} \tag{8.5}$$

The momentum per mass of fluid is called the *specific momentum* and is equal to the speed v of the fluid (relative to the observer).

Convective momentum currents are a direct consequence of the flow of fluids, so whenever we consider convective transports of (dissolved) substances or of entropy, we naturally have convective currents of momentum as well. However, we rarely have to take them into account in applications of fluid flow in small tanks and pipes (Chapter 1), in chemical flow systems, or in most open thermal systems we are going to study in Sections 8.5 and 8.6. Only when flow speeds become considerable do we have to take note of the mechanical effects. For purposes of a complete energy balance, however, the energy and momentum associated with motion will have to be taken into account (Sections 8.3.3).

8.2.3 Convective Currents of Entropy

If substances flow, the entropy stored in them flows as well. For this reason we need to know how much entropy is stored in a given fluid body. To express convective currents of entropy, the *density of entropy* stored in the fluid (ρ_S), the amount of entropy per mass (*specific entropy s*) or the entropy per amount of substance (*molar entropy* $\bar{s}$) are introduced. In uniform bodies, these are given by

$$S = \rho_S V \quad , \quad S = sm \quad , \quad S = \bar{s}n \tag{8.6}$$

respectively. The density of entropy and the entropy per mass are related by

$$\rho_S = \rho s \tag{8.7}$$

where ρ is the well known *mass density*. If we want to specify the density of entropy of a body, we shall need a constitutive theory such as the one for incompressible fluids (Chapter 4, Section 4.5) or the ideal gas (Chapter 5).

Convective entropy fluxes are calculated just like convective currents of dissolved substances. To visualize the relations, we can refer again to Fig. 8.3. Now the dots in the figure are "grains of dissolved entropy" in the fluid. A convective entropy current is the product of the entropy per volume of substance and the flux of volume of substance:

$$I_{S,conv} = \rho_S I_V \tag{8.8}$$

The other two possible expressions can be derived in a similar manner. In place of the entropy density, we use the specific entropy or the molar entropy and multiply by the flux of mass or of amount of substance, respectively:

$$I_{S,conv} = sI_m \tag{8.9}$$

$$I_{S,conv} = \bar{s}I_n \tag{8.10}$$

If necessary, we may express the fluxes in terms of mass density, speed of flow, and surface area perpendicular to the flowing substance. Note that the expressions for the convective currents only hold if the densities or specific quantities are constant across the surface.

Constitutive relations for the entropy of a fluid. Recall the relations for the specific (or the molar) entropy of a fluid. The most important examples for us are incompressible fluids such as water and ideal gases such as air. In the case of water, the molar entropy is

$$\bar{s}(T) = \bar{c}\ln\left(\frac{T}{T_{ref}}\right) \tag{8.11}$$

(Section 4.5, with $s_{ref} = 0$). $\bar{c}$ is the molar temperature coefficient of energy, the so-called molar heat capacity (do not confuse it with molar concentration, Equ.(8.1)). Note that the entropy depends only upon the temperature in the case of incompressible fluids—thermal effects are effectively de-coupled from fluid effects. This is not so for compressible fluids such as an ideal gas:

$$\bar{s}(P,T) = -R\ln\left(\frac{P}{P_{ref}}\right) + \bar{c}_P \ln\left(\frac{T}{T_{ref}}\right) \tag{8.12}$$

(see Section 5.2). The factor multiplying the logarithm of the temperatures is the temperature coefficient of enthalpy of the gas (see Equ.(5.54)). Here, pressure (or volume) effects cannot be de-coupled from the influence of temperature changes. Depending upon which of the forms of convective currents we use (i.e., those involving volume, mass, or amount of substance, Equations (8.8)-(8.10)), the expressions given here can be transformed to specific entropy or to entropy densities.

8.2.4 Energy Transfer in the Flow of Hot Pressurized Fluids

Models of physical processes make use of laws of balance of amount of substance, charge, momentum, or entropy. However, they can only be successful if we have the proper constitutive laws for flows and production rates. This is where the energy principle comes in. It restricts the form of constitutive relations; in other words, it provides much needed additional information. If we want to make use of the balance of energy in open systems, we have to formulate an expression for the energy current associated with a flow of fluid across a system boundary.

A fluid transports energy for a number of reasons: it moves, it is hot, it is under pressure and flows in a field. It may contain reactive substances, or it may be charged (just consider the plasma at the surface of the Sun). Here, I am going to investigate only the effects of temperature and pressure of a fluid (a more general expression for the energy flux will be presented in Section 8.3.3).

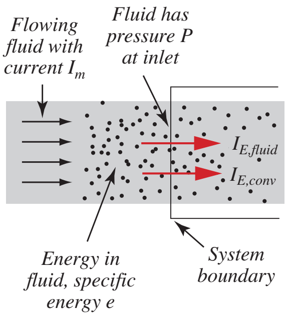

Figure 8.6: A fluid (shaded) carries a dissolved substance (dots) across the boundary of a system.

Convective energy current. Let us consider a hot fluid under pressure entering a system (Fig. 8.6). It is possible to distinguish between two contributions to the energy current. First, a fluid transports the energy stored in it (the dots is Fig. 8.6 are supposed to symbolize energy “dissolved” in the fluid) just as it transports stored entropy or momentum. This is the energy of the fluid an observer flowing along with the material would report. If we introduce the energy per volume ρ_E (energy density), the specific energy e, or the molar energy $\bar{e}$ according to

$$E = \rho_E V \quad , \quad E = em \quad , \quad E = \bar{e}n \tag{8.13}$$

we can write the convective part of the energy current as follows:

$$\begin{aligned} I_{E,conv} &= \rho_E I_V \\ I_{E,conv} &= eI_m \\ I_{E,conv} &= \bar{e}I_n \end{aligned} \tag{8.14}$$

Energy current due to a flowing pressurized fluid. Secondly, there is a term in the total energy current which we know from our study of hydraulic processes (Chapter 2). A fluid having pressure P transports an energy current equal to

$$I_{E,fluid} = PI_V \tag{8.15}$$

There are two more equivalent forms of this expression which result if we use the fluxes of mass or of amount of substance. If we replace volume by mass, the right hand side of Equ.(8.15) changes to PI_m/ρ. The inverse of the density is the *specific volume*:

$$\upsilon = 1/\rho \tag{8.16}$$

This results in

$$I_{E,fluid} = P\upsilon I_m \tag{8.17}$$

If we finally replace mass by amount of substance (by using the *molar volume* $\overline{\upsilon}$ according to Equ.(6.9)), we arrive at

$$I_{E,fluid} = P\overline{\upsilon} I_n \tag{8.18}$$

Total energy current due to flow. In the case discussed here—a hot fluid under pressure—the total energy current is simply the sum of the two contributions introduced above. If we use the current of amount of substance, we have

$$I_{E,flow} = \left(\overline{e} + P\overline{\upsilon}\right) I_n \tag{8.19}$$

The other two forms are equivalent to this and will not be written. The sum $\overline{e} + P\overline{\upsilon}$ appearing in Equ.(8.19) is normally abbreviated to the *molar enthalpy* $\overline{h}$ of the fluid (see Section 5.3.1 for a first mention of enthalpy).[4]

Constitutive relations for energy. In order to find a concrete total convective current, we obviously need the constitutive information regarding the energy of a fluid. Again, as in the case of entropy (Section 8.2.3), the forms applicable to water and air will be given. For *incompressible fluids* we have

$$\overline{e} = \overline{c}\left(T - T_{ref}\right) \tag{8.20}$$

whereas for the *ideal gas*, the molar energy is

$$\overline{e} = \overline{c}_V\left(T - T_{ref}\right) \tag{8.21}$$

Here, $e_{ref} = 0$. The molar temperature coefficient of energy is equal to coefficient of enthalpy in the case of incompressible fluids. For gases, we have to distinguish the two. Remember that for the ideal gas

$$\overline{c}_P = \overline{c}_V + R \tag{8.22}$$

where $R = 8.314$ J/(mole · K) is the universal gas constant (see Section 5.2.8 and, in particular, Equ.(5.52)).

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[4] I shall not follow the tradition at this point. As we shall shortly see (Equ.(8.20)), the energy of a fluid is usually given relative to a reference point having temperature T_{ref} and pressure P_{ref}, whereas P and υ in Equ.(8.19) are absolute values. In many applications this does not matter since differences between currents referring to the same reference state appear in laws of balance. If such differences are absent, mistakes will be made when Equ.(8.19) is applied uncritically.

8.2.5 Laws of Balance in Open Systems

The example of the transport of salt dissolved in water (Fig. 8.4) demonstrates an important aspect of flow systems. In addition to the quantities we might be interested in most directly—such as entropy or momentum if we study thermal or mechanical processes—we need to consider the balance of the flowing substances that carry entropy, momentum, or charge. In the model shown in Fig. 8.4, we see what is meant: in addition to the balance of salt, there are expressions for the balance of water in the storage elements considered. Such balances are expressed with the help of volume, mass, or amount of substance, depending upon what best suits the circumstances. In the present case, we write the law of balance of volume of water for a tank:

$$\dot{V} = \sum I_{V,i} \tag{8.23}$$

In open systems, we have to add convective currents to the processes that are responsible for changing stored quantities. Examples of such relations have already been formulated for momentum in Chapter 3 (Equ.(3.26))

$$\dot{p} = I_{p,cond} + I_{p,conv} + \Sigma_p \tag{8.24}$$

and for entropy in Chapter 7 (Equ.(7.9)):

$$\dot{S} = I_{S,cond} + I_{S,conv} + \Sigma_S + \Pi_S \tag{8.25}$$

The discussion of energy transfer in open systems in the previous section demonstrates that the balance of energy needs to be formulated slightly differently. We have to take the complete flow term into consideration, Equ.(8.19), not just what we would properly call the convective energy current (Equations (8.14)).[5] Therefore, the law of balance of energy takes the form

$$\dot{E} = I_{E,cond} + I_{E,flow} + \Sigma_E \tag{8.26}$$

QUESTIONS

1. Why does pouring hot water out of a container not change the temperature of the water that remains in the tank? Why does letting cold water flow into a tank with hot water lower the temperature of the water in the container?
2. What is the specific momentum of a fluid?
3. Why do we have to consider more than the energy stored in a fluid (the internal energy e) when calculating the energy current due to the flow of a fluid into or out of a system?
4. Imagine a compressed spring being pushed into a containment. The containment is our control volume for analysis. Consider the total energy current due to the spring entering the containment (i.e., the energy current due to the "flow" of the spring across the surface of the control volume). Is there a part of the total energy current associated with the spring that resembles the flow of stored energy (eI_m, Equ.(8.14)$_2$)? Is there a part that resembles the expression $P\upsilon I_m$ in Equ.(8.17)?
5. Why is it not necessary to distinguish between temperature coefficients of energy and of

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[5] In Chapter 7 (Equ.(7.10)), the fluid or hydraulic term $P\upsilon I_m$ was not yet included.

enthalpy, C_V and C_P, in the case of incompressible fluids (such as in Equ.(8.20))?

6. Consider two communicating tanks with an additional outflow as in Fig. 8.4. There is a little bit of hot water in Tank 1 and a lot of cold water in Tank 2. How will the temperatures of the water in the two tanks behave over the course of time? (Assume the tanks to be thermally insulated.)

EXAMPLE 8.1. Convective currents with water.

Water at a temperature of 50°C is flowing through a pipe whose diameter is 5.0 cm. The mass flux is 10 kg/s. Calculate the magnitude of (a) the convective current of entropy, and (b) the convective current of momentum (compare to the conductive momentum current for a pressure of 1.0 bar).

SOLUTION: (a) If we choose to base the calculation on the flux of mass, we need the entropy per mass of the fluid, which is given by

$$s(T) = s\left(T_{ref}\right) + c\ln\left(\frac{T}{T_{ref}}\right) = 0 + 4200 \cdot \ln\left(\frac{323}{273}\right) = 706\frac{\mathrm{J}}{\mathrm{K}\cdot\mathrm{kg}}$$

In mechanical engineering, $s(T_{ref})$ is often set equal to zero for $T_{ref} = 273$ K (alternatively, we could have taken the absolute value of the entropy from the tables for the chemical potential and its temperature coefficient, Table 6.2). The convective flux of entropy follows from Equ.(8.9):

$$\left|I_{s,conv}\right| = s(T)\left|I_m\right| = 706 \cdot 10\frac{\mathrm{W}}{\mathrm{K}} = 7.06 \cdot 10^3\,\frac{\mathrm{W}}{\mathrm{K}}$$

The remarks above concerning reference values show that we cannot apply absolute meaning to the numerical values obtained here. (The same would be true if we wanted to calculate flow energy currents.) The problem is commonly resolved by considering differences of inflows and outflows relative to the same reference point (see Example 8.2).

(b) We need to know the speed of flow in order to calculate the convective momentum current. This follows from the flux of mass (or volume) and the cross section of the pipe:

$$\left|I_m\right| = \rho\left|I_V\right| = \rho A v \quad \Rightarrow \quad v = 5.1\,\mathrm{m/s}$$

The current of momentum is the product of the momentum per mass (the speed) and the mass flux:

$$\left|I_{p,conv}\right| = v\left|I_m\right| = 51\,\mathrm{N}$$

If the pressure of the water is 1 bar, the value of the convective momentum flux is a sizeable fraction of the conductive momentum current ($I_{p,cond} = AP = \pi \cdot 0.025^2 \cdot 1.0 \cdot 10^5$ N $= 200$ N).

EXAMPLE 8.2. Net convective entropy and flow energy currents with air.

Imagine a current of air of 100 mole/s flowing through a technical device. At the entrance, pressure and temperature of the air are 2.0 bar and 400 K. At the exit, the values are 1.0 bar and 300 K, respectively. Neglect kinetic energy terms. (a) Calculate the net convective entropy current and (b) the net energy current due to the flow of the air through the device. (c) Is it possible to have such a situation?

SOLUTION: (a) The (molar) entropy of air can be approximated by the ideal gas model (see Equ.(8.12)) with a molar temperature coefficient of enthalpy of 7/2*R* (according to the results of Chapter 5, the adiabatic exponent of air is close to 1.4). The reference values of pressure and temperature do not matter because we take differences of inlet and outlet conditions:

$$I_{S,conv,net} = \left(\bar{s}_{in} - \bar{s}_{out}\right) I_n = \left[-R \ln\left(\frac{P_{in}}{P_{out}}\right) + \bar{c}_P \ln\left(\frac{T_{in}}{T_{out}}\right) \right] I_n$$

$$= \left[-8.314 \cdot \ln(1/2) + 3.5 \cdot 8.314 \cdot \ln(400/300) \right] \cdot 100 \frac{\text{W}}{\text{K}} = 1.41 \cdot 10^3 \frac{\text{W}}{\text{K}}$$

(b) Again, the reference state will not matter here since we take differences of currents. The net flow energy current is calculated with the help of Equ.(8.19), Equ.(8.21), Equ.(8.22), and the equation of state of the ideal gas:

$$\begin{aligned} I_{E,flow,net} &= \left[\left(\bar{e} + P\bar{v}\right)_{in} - \left(\bar{e} + P\bar{v}\right)_{out} \right] I_n \\ &= \left[\left(\bar{e}_{in} - \bar{e}_{out}\right) + \left[\left(P\bar{v}\right)_{in} - \left(P\bar{v}\right)_{out} \right] \right] I_n \\ &= \left[\bar{c}_V \left(T_{in} - T_{out}\right) + \left[(RT)_{in} - (RT)_{out} \right] \right] I_n \\ &= \bar{c}_P \left(T_{in} - T_{out}\right) I_n = 3.5 \cdot 8.314 \cdot (400 - 300) \cdot 100\text{W} = 291\text{kW} \end{aligned}$$

(c) Laws of balance for entropy and energy can tell us if the flow process described here is possible at all. Let us assume a steady-state flow. There is more entropy flowing in than out with the air, so the air must be cooled by an entropy current equal to – 1.41 kW/K. If we estimate the energy current associated with this cooling by assuming an average temperature of 350 K, the conductive energy flow is roughly – 500 kW.

Since the energy flow with air coming in is greater by only 291 kW than the one exiting with air, we would still have to add energy from outside at a rate of roughly 200 kW. This may not happen by heating because that would mean that we would have to remove still more entropy. It appears that the only possibility is to compress the air mechanically. (Whether or not this is technically feasible and sensible is an altogether different question.)

8.3 ANALYSIS OF IDEAL FLOW SYSTEMS

This section is devoted to a more detailed study of laws of balance and the energy principle in flow systems. Here, the expression for the energy current due to the flow of a fluid will be generalized, and dynamical balances will be considered. This will lead to two important results: a general form of the chemical potential of fluids and the Gibbs Fundamental Form for specific or molar quantities. The expression for the chemical potential and the enthalpy of fluids will be applied to incompressible fluids and the ideal gas in Section 8.4.

8.3.1 Analysis of a Flow System Excluding Mechanical Effects

A flow system that is somewhat more general than the one depicted in Fig. 8.6 is shown in Fig. 8.7. We consider a (compressible) fluid in a control volume where part of the surface is open to the flow of the fluid, and part is closed but movable. The latter element allows for volume changes or the addition of what have been called compressive processes. The fluid entering at the open surface has the same instantaneous pressure and temperature as the fluid inside. Excluding mechanical effects means that we do not consider momentum and momentum transfers, and we assume that the (center of mass) of the fluid in the system does not move. Mechanical processes will be included in the analysis in Section 8.3.3.

Laws of balance. There are three extensive quantities to be taken into account: amount of substance, entropy, and volume. The laws of balance for these quantities are

$$\begin{aligned} \dot{n} &= I_n \\ \dot{S} &= I_{S,conv} + I_{S(c)} \\ \dot{V} &= \Pi_V \end{aligned} \qquad \textbf{(8.27)}$$

The second relation (for entropy) expresses the assumptions that the fluid flowing in carries entropy, and that there is heating (leading to a *conductive* current of entropy, $I_{S(c)}$). There is no dissipation, however. This follows from the other assumptions of the model (no jumps of pressure or temperature at the open surface; spatial homogeneity; no internal friction).

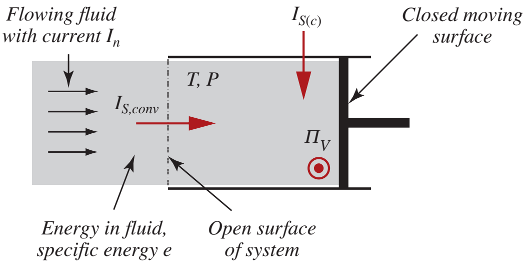

Figure 8.7: A system having both an open surface across which matter can flow, and a movable closed wall which serves to compress or expand the fluid contained in the system. Π_V is the rate of production of volume.

The balance of energy can be assembled from what we have discussed so far: there is heating, volume change, and flow:

$$\dot{E} = I_{E,flow} + I_{E,th} + I_{E,comp} \qquad \textbf{(8.28)}$$

where the first term will be expressed with the help of Equ.(8.19). The second and third terms will be formulated below.

Constitutive relations and energy currents. There are a number of terms in the previous laws of balance that depend upon particular circumstances. There is the convective current of entropy

$$I_{S,conv} = \bar{s} I_n \qquad \textbf{(8.29)}$$

then there are the energy currents:

$$\begin{aligned} I_{E,flow} &= \left(\bar{e} + P\bar{v}\right) I_n \\ I_{E,th} &= T\, I_{S(c)} \\ I_{E,comp} &= -P\,\Pi_V \end{aligned} \qquad \textbf{(8.30)}$$

Finally, we shall make use of the relation that introduces the chemical potential of the fluid to interpret the results that follow from all the above relations:

$$I_{E,chem} = \mu I_n \tag{8.31}$$

Evaluation of the relations. Both the constitutive relations and the laws of balance of amount of substance, entropy, and volume (Equ.(8.27)) will be inserted in the balance of energy. This leads to

$$\begin{aligned}\dot{E} &= I_{E,flow} + I_{E,th} + I_{E,comp}\\ &= \left(\bar{e} + P\bar{v}\right)I_n + T\,I_{S(c)} - P\Pi_V\\ &= \left(\bar{e} + P\bar{v}\right)I_n + T\left(\dot{S} - I_{S,conv}\right) - P\dot{V}\\ &= \left(\bar{e} + P\bar{v}\right)I_n - T\,I_{S,conv} + T\,\dot{S} - P\dot{V}\\ &= \left(\bar{e} + P\bar{v} - T\,\bar{s}\right)I_n + T\,\dot{S} - P\dot{V}\end{aligned}$$

Now we interpret the first term as the energy current due to chemical processes, i.e., processes having to do with substances. If we use Equ.(8.31) and replace I_n by the rate of change of amount of substance (according to the law of balance Equ.$(8.27)_{(1)}$), we finally have

$$\dot{E} = \mu\dot{n} + T\,\dot{S} - P\dot{V} \tag{8.32}$$

and

$$\mu = \bar{e} + P\bar{v} - T\,\bar{s} \tag{8.33}$$

The first of these relations is the Gibbs Fundamental form for our particular model and the second tells us how we can obtain the chemical potential of a fluid of the type considered here. The GFF is the same as that for the ideal fluid studied in Chapter 5 with the exception of the addition of the term relating to changes of amount of substance. This addition is the result of the fact that we now deal with open systems that exchange matter with their surroundings: the amount of substance of the system is no longer constant.

The results have been derived for reversible processes. It will be interesting to see in Chapters 10-12 that they also hold for materials capable of irreversible changes as long as the processes are still relatively simple (diffusion of entropy, substances, or charge, diffusion of momentum, i.e., friction, etc.) and not too fast.

8.3.2 The Gibbs Fundamental Form for Specific or Molar Quantities

Using simple algebra, we can prove that the Gibbs Fundamental Form, Equ.(8.32), also holds for specific or molar quantities, i.e., for molar energy, entropy, and volume. Using the latter, we have

$$E = \bar{e}\,n \quad , \quad S = \bar{s}\,n \quad , \quad V = \bar{v}\,n \tag{8.34}$$

These expressions are introduced in Equ.(8.32) which leads to

$$\left[\dot{\bar{e}} - T\,\dot{\bar{s}} + P\dot{\bar{v}}\right]n = \left[\mu - \bar{e} - P\bar{v} + T\,\bar{s}\right]\dot{n}$$

Since *dn/dt* and *n* can be changed independently, this equation is satisfied only if both factors in brackets are equal to zero. On the right, we obtain what we already know, namely how to calculate the chemical potential of the fluid (Equ.(8.33)). The left hand side, however, furnishes a new result:

$$\dot{\bar{e}} = T\dot{\bar{s}} - P\dot{\bar{v}} \tag{8.35}$$

This is the GFF of the simple fluids considered in terms of molar quantities of energy, entropy, and volume. It can also be obtained for the specific values and looks just the same. These are examples of expressions that will also be derived in continuum thermodynamics (see Chapters 11-12).

8.3.3 Flow Systems Including Mechanical Effects

When mechanical effects are included in the model of a flow system, a number of things change—a few equations and terms need to be added to the analysis already presented.

First among these is the equation of balance of momentum which includes a convective term; then we have to augment the energy of the fluid by the kinetic energy term. Finally, there is one more energy transfer to be considered, namely, the one with radiative or conductive momentum transfer (see Chapter 3). The additional quantities are shown in Fig. 8.8. In the following, the analyses of Sections 8.3.1 and 8.3.2 will be repeated and the new parts explained.

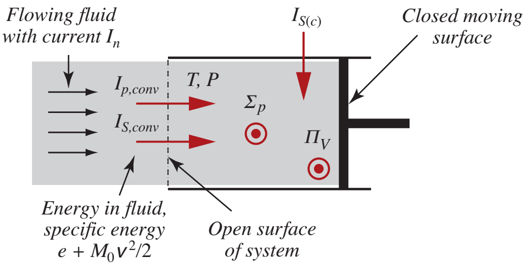

Figure 8.8: A fluid carries entropy and momentum into a system. The fluid in the system can be compressed (Π_V) and heated ($I_{S(c)}$). At the same time, momentum is exchanged by interaction with a field (Σ_p).

Laws of balance. There are now four extensive quantities to be taken into account: amount of substance, entropy, volume, and momentum. The laws of balance for the first three are the same as in Equ.(8.27). For momentum we have

$$\dot{p} = I_{p,conv} + \Sigma_p \tag{8.36}$$

if we let the additional mechanical interaction be radiative, i.e., due to a field. A conductive term will work out in the same manner, so it does not have to be added separately.[6]

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[6] Actually, there is a conductive term due to the compressive state (and the compression or expansion) of the gas. Remember that compression of expansion can be treated as a mechanical process (Section 3.5.3).

The balance of energy receives an additional term which results from the non-convective transfer of momentum which is radiative in the example discussed in this section (see Fig. 8.8):

$$\dot{E} = I_{E,flow} + I_{E,th} + I_{E,comp} + I_{E,mech} \tag{8.37}$$

Constitutive relations and energy currents. One of the important differences comes from the (specific or molar) energy of the fluid. In addition to the term which is called specific or molar energy, e or $\bar{e}$, there will be the energy of the moving body, again calculated per mass or per amount of substance. The kinetic energy per mass is simply one half times the speed squared. To obtain the molar quantity, we multiply by the molar mass M_0. The energy per amount of substance therefore equals

$$\bar{e} = \bar{e}^{(i)} + \frac{1}{2} M_0 v^2 \tag{8.38}$$

$\bar{e}^{(i)}$ is the *intrinsic part of the (molar) energy* of the fluid, what I previously called the molar energy $\bar{e}$.

In addition to the convective current of entropy, Equ.(8.29), we have to include a convective momentum current

$$I_{p,conv} = \bar{p} I_n = M_0 v I_n \tag{8.39}$$

New among the energy currents are the expressions for the flow energy

$$I_{E,flow} = \left(\bar{e}^{(i)} + \frac{1}{2} M_0 v^2 + P\bar{\upsilon} \right) I_n \tag{8.40}$$

and the mechanical energy current

$$I_{E,mech} = v \Sigma_p \tag{8.41}$$

Evaluation of the relations. The information assembled here can be combined by inserting constitutive relations and laws of balance into the balance of energy:

$$\begin{aligned}
\dot{E} &= I_{E,flow} + I_{E,th} + I_{E,comp} + I_{E,mech} \\
&= \left(\bar{e}^{(i)} + M_0 v^2/2 + P\bar{\upsilon} \right) I_n + T I_{S(c)} - P \Pi_V + v \Sigma_p \\
&= \left(\bar{e}^{(i)} + M_0 v^2/2 + P\bar{\upsilon} \right) I_n + T\left(\dot{S} - I_{S,conv} \right) - P\dot{V} + v\left(\dot{p} - I_{p,conv} \right) \\
&= \left(\bar{e}^{(i)} + M_0 v^2/2 + P\bar{\upsilon} - T\bar{s} - M_0 v^2 \right) I_n + T\dot{S} - P\dot{V} + v\dot{p} \\
&= \left(\bar{e}^{(i)} + P\bar{\upsilon} - T\bar{s} - M_0 v^2/2 \right) I_n + T\dot{S} - P\dot{V} + v\dot{p}
\end{aligned}$$

According to Equ.(8.31), the first term in parentheses equals the chemical potential of the fluid. This then results in

$$\dot{E} = \mu \dot{n} + T\dot{S} - P\dot{V} + v\dot{p} \tag{8.42}$$

and

$$\mu = \bar{e}^{(i)} + P\bar{\upsilon} - T\bar{s} - \frac{1}{2}M_0 v^2 \tag{8.43}$$

Again, the first of these equations is the Gibbs Fundamental form. Notice that it differs from Equ.(8.32) by the term involving the rate of change of the momentum of the system. Equ.(8.43) shows that the chemical potential of a fluid decreases with decreasing speed.

The Gibbs Fundamental Form. The Gibbs Fundamental Form, Equ.(8.42), also holds for specific or molar quantities, i.e., for molar energy, entropy, and volume. Molar quantities are

$$E = \left(\bar{e}^{(i)} + M_0 v^2/2\right)n \quad , \quad S = \bar{s}n \quad , \quad V = \bar{\upsilon}n \quad , \quad p = \bar{p}n \tag{8.44}$$

These expressions are introduced in Equ.(8.42) which leads to

$$\left[\dot{\bar{e}} + M_0 v\dot{v} - T\dot{\bar{s}} + P\dot{\bar{\upsilon}} - v\dot{\bar{p}}\right]n = \left[\mu - \left(\bar{e}^{(i)} + M_0 v^2/2\right)e - P\bar{\upsilon} + T\bar{s} + v\bar{p}\right]\dot{n}$$

Using the same argument as before regarding the independence of *n* and *dn/dt*, we find that

$$\dot{\bar{e}} = T\dot{\bar{s}} - P\dot{\bar{\upsilon}} \tag{8.45}$$

The GFF expressed with molar quantities has not changed from the result derived before in Equ.(8.35).

QUESTIONS

7. Are the terms $P\upsilon I_n$ in Equ.(8.30)$_{(1)}$ and $P\Pi_V$ in Equ.(8.30)$_{(2)}$ the same (due to the same process) or do they refer to different phenomena?
8. If we hold a gas under pressure, momentum flows across its surface. Why is it still possible to neglect mechanical phenomena (such as in the case discussed in Section 8.3.1)?
9. Why does it make sense that the GFF expressed in molar (or specific) quantities is the same for systems that do or do not include mechanical effects? (See Equ.(8.35) and Equ.(8.45).)

EXAMPLE 8.3. Flow of an ideal incompressible fluid: Bernoulli's law.

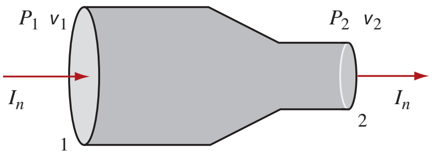
Derive the expression for the dependence of pressure on the speed of flow for the case of an incompressible ideal fluid, without exchange of energy with the environment.

SOLUTION: The law of balance of energy for the fluid system between points 1 and 2 (see the accompanying Fig. Ex.3) follows from Equ.(8.40):

$$e^{(i)} + \frac{P_1}{\rho} + \frac{1}{2}v_1{}^2 = e^{(i)} + \frac{P_2}{\rho} + \frac{1}{2}v_2{}^2$$

This follows from our assumption that there is no exchange of energy with the surroundings; therefore, the only currents of energy with respect to the system considered are the fluxes associated with fluid flow at the inlet and the outlet of the system.

Figure Ex.3



Since the flow is ideal, there will not be any production of entropy between points 1 and 2. Equal density of entropy of the incompressible fluid at the inlet and the outlet finally means that the temperature of the fluid must remain constant. This, in turn, implies constant internal energy. Therefore we find that:

$$P_1 + \frac{1}{2}\rho v_1^{\,2} = P_2 + \frac{1}{2}\rho v_2^{\,2}$$

This relation is what physicists normally call Bernoulli's Law (for horizontal flow). Historically, it was derived on the basis of the momentum equation along a flow line of a fluid, not on the balance of energy (the energy principle entered physics much later).

EXAMPLE 8.4. Measuring the temperature coefficient of enthalpy of air.

In Example 5.10 of Chapter 5, a way of measuring the "heat capacity at constant pressure", i.e., the temperature coefficient of enthalpy, was presented on the basis of a closed systems analysis. (a) Derive the same result using the control volume approach. (b) Estimate the magnitude of the velocity term in the expression for the flow energy current.

SOLUTION: (a) We have three energy currents with respect to the vertical pipe in which heated air is rising. Therefore, the equation of balance takes the form

$$-\left|U_{el} I_q\right| + h_1 I_{m1} + h_2 I_{m2} = 0$$

h is the specific enthalpy. Here, the velocity term has been neglected. If the temperature coefficient of enthalpy increases linearly with temperature, the coefficient can be estimated by

$$c_P = \frac{h_2 - h_1}{T_2 - T_1} = \frac{1}{T_2 - T_1}\frac{\left|U_{el} I_q\right|}{\left|I_m\right|}$$

with

$$I_m = \rho_2 A v_2 = \frac{M_0 P}{R T_2} A v_2$$

(b) The speed of flow will be of the order of a few meters per second, which gives the change of the velocity term in Equ.(8.40) a magnitude of less than 100 m^2/s^2 between the bottom and the top of the pipe. The change of the enthalpy, on the other hand, has a magnitude of about 100 K · 1000 J/(K · kg) so we are justified in neglecting the kinetic energy of the fluid.

EXAMPLE 8.5. Isothermal compressors.

Air (modeled as an ideal gas) flows through a compressor (driven by a rotational process supplying energy at a certain rate) at a steady rate. We desire the air to have the same temperature at the outlet as at the inlet. (a) Demonstrate using a control volume analysis that the air has to be cooled and that the energy current due to cooling equals the mechanical energy current. (b) Demonstrate that the process is reversible (assume there to be no friction).

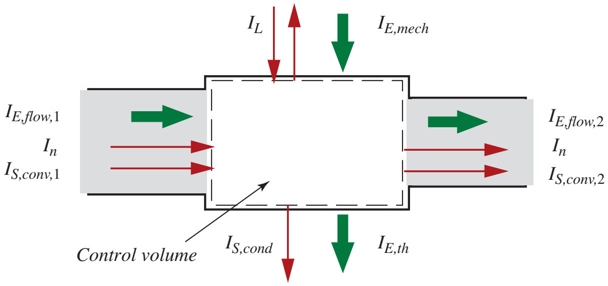


Figure Ex.5: Control volume analysis of an (isothermal) compressor. It includes both conductive and convective currents of entropy. I_L denotes the flux of angular momentum.

(a) The steady-state expression for the balance of energy of the control volume in Fig. Ex.5.1 includes terms for flow, and mechanical and thermal processes:

$$\left(\bar{e}_1 + P_1\bar{\upsilon}_1\right)I_{n1} + I_{E,mech} + I_{E,cooling} + \left(\bar{e}_2 + P_2\bar{\upsilon}_2\right)I_{n2} = 0$$

Rearranging the terms leads to

$$\begin{aligned} I_{E,mech} + I_{E,cooling} &= \left(\bar{e}_2 - \bar{e}_1 + P_2\bar{\upsilon}_2 - P_1\bar{\upsilon}_1\right)\left|I_n\right| \\ &= \left(\bar{e}_2 - \bar{e}_1 + RT - RT\right)\left|I_n\right| \\ &= \left(\bar{e}_2 - \bar{e}_1\right)\left|I_n\right| = 0 \end{aligned}$$

The equation of state of the ideal gas was used to obtain the second line. For the final result we made use of the fact that the energy of the ideal gas depends only upon temperature (which is the same at the inlet and the outlet).

(b) The steady-state balance of entropy is

$$\Pi_S + I_{S,cond} + \left[-R\ln\left(P_1/P_2\right) + \bar{c}_P\ln\left(T_1/T_2\right)\right]I_{n1} = 0$$

The last term drops out since the temperatures are the same. The entropy current in cooling is obtained from the energy current $I_{E,cool}$ by dividing the latter by T. Since the energy current in cooling equals the mechanical energy flux, we have

$$\Pi_S = \frac{1}{T}I_{E,mech} - R\ln\left(P_2/P_1\right)I_{n1}$$

If we want to compress a certain amount of an ideal gas at constant temperature, the energy needed is calculated according to

$$E_{mech} = nRT\ln\left(P_2/P_1\right)$$

(see Chapter 5). For a constant stream of air, we get the energy current needed if we replace the amount of substance by the flux of this quantity:

$$\left|I_{E,mech}\right| = RT\ln\left(P_2/P_1\right)\left|I_n\right|$$

If we combine this with the expression for the production rate of entropy, we obtain a result of zero. The model considered here is one of reversible processes.

8.4 PROPERTIES OF SIMPLE FLUIDS

We are now in a position to say more about thermo-chemical properties of simple fluids such as water or air that are modeled as either incompressible liquids or as an ideal gas. In particular, we can use the relation between energy, entropy, and volume and the chemical potential to learn more about the latter. One important result concerns the temperature and pressure coefficients of the chemical potential that were already used in Chapter 6.

8.4.1 The Chemical Potential and Molar Enthalpy of Uniform Fluids

Expressions for the chemical potential of ideal fluids were obtained in the previous sections, see Equ.(8.33) and Equ.(8.43). In this section, the form excluding mechanical effects, i.e.,

$$\mu = \bar{e} + P\bar{\upsilon} - T\bar{s} \tag{8.46}$$

will be used to derive the chemical potential of incompressible fluids and the ideal gas as functions of temperature and pressure. It is common to use the abbreviation

$$\bar{h} = \bar{e} + P\bar{\upsilon} \tag{8.47}$$

in the expression for the chemical potential which leads to

$$\mu = \bar{h} - T\bar{s} \tag{8.48}$$

$\bar{h}$ is the *molar enthalpy* of the fluid (remember the brief introduction to enthalpy in Section 5.3, Equ.(5.70)). Some of the results that shall be listed here were already obtained in Chapter 6.

8.4.2 Incompressible Fluids

Let us begin by listing the properties of incompressible fluids that have been derived so far: the molar volume is constant, the energy depends only on the temperature, and so does the entropy:

$$\begin{aligned} &\bar{\upsilon} = const. \\ &\bar{e} = \bar{c}\left(T - T_{ref}\right) + \bar{e}_{ref} \\ &\bar{s} = \bar{c}\ln\left(T/T_{ref}\right) + \bar{s}_{ref} \end{aligned} \tag{8.49}$$

These expressions are used to derive the molar enthalpy (Equ.(8.47)) and the chemical potential (Equ.(8.46)). For the former we have

$$\begin{aligned} \bar{h} - \bar{h}_{ref} &= \left(\bar{e} - \bar{e}_{ref}\right) + \left[\left(P\bar{\upsilon}\right) - \left(P\bar{\upsilon}\right)_{ref}\right] \\ &= \left(\bar{e} - \bar{e}_{ref}\right) + \left(P - P_{ref}\right)\bar{\upsilon} \end{aligned}$$

which leads to

$$\bar{h} - \bar{h}_{ref} = \bar{c}\left(T - T_{ref}\right) + \left(P - P_{ref}\right)\bar{\upsilon} \tag{8.50}$$

The chemical potential can be obtained by subtracting the product of temperature and molar entropy:

$$\begin{aligned}\mu - \mu_{ref} &= \left[\bar{h} - T\,\bar{s}\right] - \left[\bar{h} - T\,\bar{s}\right]_{ref} \\ &= \bar{h} - \bar{h}_{ref} - \left[T\,\bar{s} - T_{ref}\bar{s}_{ref}\right] \\ &= \bar{h} - \bar{h}_{ref} - \left[T\left(\bar{s} - \bar{s}_{ref}\right) + \left(T - T_{ref}\right)\bar{s}_{ref}\right]\end{aligned}$$

Inserting Equ.(8.50) and the expression for the entropy, the chemical potential of an incompressible fluid as a function of pressure and temperature becomes

$$\mu - \mu_{ref} = \bar{c}\left(T - T_{ref}\right) + \left(P - P_{ref}\right)\bar{\upsilon} - T\,\bar{c}\,\ln\left(\frac{T}{T_{ref}}\right) - \left(T - T_{ref}\right)\bar{s}_{ref} \tag{8.51}$$

Note that we need to know the absolute value of the entropy at the reference state to calculate chemical potentials.

8.4.3 The Ideal Gas

The derivations proceed along the same lines as for incompressible fluids. First, we have to list the properties of the ideal gas:

$$\begin{aligned}&P\bar{\upsilon} = RT \\ &\bar{e} = \bar{c}_V\left(T - T_{ref}\right) + \bar{e}_{ref} \\ &\bar{s} = -R\ln\left(P/P_{ref}\right) + \bar{c}_P\,\ln\left(T/T_{ref}\right) + \bar{s}_{ref}\end{aligned} \tag{8.52}$$

The first relation is the equation of state written for the molar volume, the second tells us that the energy depends only upon the temperature, and the third has been formulated for temperature and pressure as independent variables (see Chapter 5). Now the enthalpy turns out to be

$$\begin{aligned}\bar{h} - \bar{h}_{ref} &= \left(\bar{e} - \bar{e}_{ref}\right) + \left[\left(P\bar{\upsilon}\right) - \left(P\bar{\upsilon}\right)_{ref}\right] \\ &= \bar{c}_V\left(T - T_{ref}\right) + R\left(T - T_{ref}\right)\end{aligned}$$

which means that

$$\bar{h} - \bar{h}_{ref} = \bar{c}_P\left(T - T_{ref}\right) \tag{8.53}$$

The derivation of the chemical potential as a function of pressure and temperature follows the same steps as before:

$$\mu - \mu_{ref} = \bar{h} - \bar{h}_{ref} - \left[T\left(\bar{s} - \bar{s}_{ref}\right) + \left(T - T_{ref}\right)\bar{s}_{ref}\right]$$

which, with the help of the entropy in Equ.(8.52) leads to

$$\mu - \mu_{ref} = \bar{c}_P\left(T - T_{ref}\right) + RT \ln\left(\frac{P}{P_{ref}}\right) - T\,\bar{c}_P \ln\left(\frac{T}{T_{ref}}\right) - \left(T - T_{ref}\right)\bar{s}_{ref} \tag{8.54}$$

We can easily derive expression where either pressure or temperature are kept constant if we would like to know the dependence of enthalpy or the chemical potential upon pressure or temperature only.

8.4.4 Temperature and Pressure Coefficients of Chemical Potentials

In Section 6.4.4, I introduced the coefficients used in the linear approximation of the chemical potential as a function of temperature and pressure. If you inspect Equ.(6.24) and Equ.(6.25), you will see that they correspond to the partial derivatives of the chemical potential with respect to temperature or pressure. Here, we will derive them for the special cases treated in the paragraphs above. Starting with the pressure coefficient, the results for incompressible fluids and the ideal gas lead to the same general expression:

$$\beta_\mu \equiv \left.\frac{\partial \mu(T,P)}{\partial P}\right|_{T=T_{ref}} = \bar{\upsilon}_{ref} \tag{8.55}$$

The pressure coefficient corresponds to the molar volume of the fluid. The case of the temperature coefficient is a little bit more complicated. Evaluation of the derivative of Equ.(8.54) with respect to temperature at $T = T_{ref}$ shows that

$$\alpha_\mu \equiv \left.\frac{\partial \mu(T,P)}{\partial T}\right|_{T=T_{ref}} = \left[\bar{c}_p - \bar{c}_p \ln\left(\frac{T}{T_{ref}}\right) - T\,\bar{c}_p \frac{T_{ref}}{T}\frac{1}{T_{ref}} - \bar{s}_{ref}\right]_{T=T_{ref}}$$

which becomes

$$\alpha_\mu \equiv -\bar{s}_{ref} \tag{8.56}$$

(Equ.(8.51) leads to the same result.) The temperature coefficient is equal to the negative molar entropy of the reference state. In Chapter 10, it will be demonstrated that these results hold not only for the fluids investigated here, and not just for the reference state. For now they are enough to clarify some features of the tabulated values of chemical potentials we have been using in our examples (Table 6.4). They show that the chemical potential increases with pressure at constant temperature, and it decreases with temperature at constant pressure (Equ.(6.32)).

QUESTIONS

10. If the temperature is changed in an incompressible fluid, how does the pressure change?
11. Energy and enthalpy of the ideal gas appear to depend only upon the temperature. Does this mean they cannot be changed when the pressure of a gas changes?
12. How could the absolute entropy of water at 50°C be calculated?

8.5 IRREVERSIBILITY IN FLOW SYSTEMS

As in any other system, sources of irreversibility are always present. When fluids flow, there is friction, and they undergo the typical irreversible processes that take place in fluids at rest as well (absorption of radiation, chemical reactions, diffusion of electricity, heat, and substances). In flow systems, there is an additional entropy producing process, namely, *mixing of fluids* at different temperatures and pressures that will now be investigated. A further entropy producing flow phenomenon is the so-called *throttling process* where a fluid expands and its pressure is relaxed during flow through a porous plug; this will be described further in Section 8.6.3 below.

8.5.1 Analysis of a Flow Heater

To demonstrate the usefulness of the analysis of flow systems, consider a fluid such as water or air flowing through a duct as it is heated. The heating may be solar as in a thermal solar collector, or it may be conventional from burning fuel or an electric heater (Fig. 8.9). There is an entropy current I_S due to heating accompanied by a flux of energy, $I_{E,th}$. At the inlet of the duct, the fluid has temperature T_i and pressure P_i; where it leaves the duct, temperature and pressure are T_o and P_o, respectively.

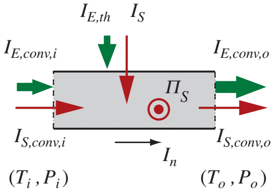


Figure 8.9: A flow heater. A fluid flows through a duct (current I_n). Heating is quantified by I_S, $I_{E,th}$. The fluid enters with values (T_i,P_i) and exits at (T_o,P_o).

Steady-state balances. If we operate the heater in steady-state, the laws of balance of entropy and energy are expressed as follows:

$$0 = I_S + I_{S,conv,i} + I_{S,conv,o} + \Pi_S \tag{8.57}$$

$$0 = I_{E,th} + I_{E,flow,i} + I_{E,flow,o} \tag{8.58}$$

Let us evaluate the balance of energy. The current due to heating is assumed to be known. The expressions for flow energy are given by Equ.(8.19) and Equ.(8.21):

$$I_{E,th} + \bar{c}_V\left(T_i - T_{ref}\right)I_n + P_i\bar{\upsilon}_i I_n = \bar{c}_V\left(T_o - T_{ref}\right)I_n + P_o\bar{\upsilon}_o I_n$$

which is equivalent to

$$I_{E,th} = \bar{c}_V\left(T_o - T_i\right)I_n + \left(P_o\bar{\upsilon}_o - P_i\bar{\upsilon}_i\right)I_n \tag{8.59}$$

Incompressible fluids. The last expression can be adapted to the case of incompressible fluids such as water. Here, the temperature coefficient of energy is c, and the specific or molar volumes are the same at the inlet and at the outlet. In steady-state, the energy current due to heating must therefore be equal to

$$I_{E,th} = \bar{c}\left(T_o - T_i\right)I_n + \left(P_o - P_i\right)\bar{\upsilon}I_n \tag{8.60}$$

This allows us to find the entropy production rate with the help of the equation of balance of entropy (Equ.(8.57)):

$$\Pi_S = -\left(I_S + I_{S,conv,i} + I_{S,conv,o}\right)$$

With the help of Equ.(8.60) and Equ.(8.11), this leads to

$$\Pi_S = -\frac{1}{T_o}\left(\bar{c}\left(T_o - T_i\right)I_n + \left(P_o - P_i\right)\bar{\upsilon}I_n\right) \\ -\left(\bar{c}\ln\left(\frac{T_i}{T_{ref}}\right) - \bar{c}\ln\left(\frac{T_o}{T_{ref}}\right)\right)I_n$$

which then leads to

$$\Pi_S = \frac{1}{T_o}\left[\bar{c}\left(T_i - T_o\right) - T_o\bar{c}\ln\left(\frac{T_i}{T_o}\right) + \bar{\upsilon}\left(P_i - P_o\right)\right]I_n \tag{8.61}$$

The ideal gas. The analysis of a simple gas flowing through a heater proceeds analogously. Now, we make use of the equation of state of the ideal gas, $PV = nRT$ or $P\bar{\upsilon} = RT$. Equ.(8.60) changes to

$$I_{E,th} = \bar{c}_V\left(T_o - T_i\right)I_n + \left(RT_o - RT_i\right)I_n \\ = \left(\bar{c}_V + R\right)\left(T_o - T_i\right)I_n$$

With Equ.(8.22), we have the final result

$$I_{E,th} = \bar{c}_P\left(T_o - T_i\right)I_n \tag{8.62}$$

This form is of particular interest. It tells us that if the temperature of a body of ideal gas changes from T_i to T_o, and its pressure from P_i to P_o, the amount of energy transferred in heating or cooling equals the temperature difference multiplied by the temperature coefficient of enthalpy.

Now we can return to the equation of balance of entropy and determine the entropy production rate for this process:

$$\Pi_S = -\left(I_S + I_{S,conv,i} + I_{S,conv,o}\right)$$

Insertion of the constitutive relations yields

$$\Pi_S = -\frac{1}{T_o}I_{E,th} - \left(-R\ln\left(\frac{P_i}{P_{ref}}\right) + \bar{c}_P\ln\left(\frac{T_i}{T_{ref}}\right)\right)I_n \\ + \left(-R\ln\left(\frac{P_o}{P_{ref}}\right) + \bar{c}_P\ln\left(\frac{T_o}{T_{ref}}\right)\right)I_n$$

With Equ.(8.62) and Equ.(8.12), the result is

$$\Pi_S = -\frac{1}{T_o}\bar{c}_P\left(T_o - T_i\right)I_n - \left(-R\ln\left(\frac{P_i}{P_o}\right) + \bar{c}_P\ln\left(\frac{T_i}{T_o}\right)\right)I_n \tag{8.63}$$

Using the enthalpy. In steady-state flow systems analysis of the type we are studying here, it is quite common to use the enthalpy of a fluid to abbreviate the expressions.

The constitutive law for flow energy is then

$$I_{E,flow} = \bar{h} I_n \tag{8.64}$$

where Equ.(8.50) and Equ.(8.53) provide the concrete expressions for the enthalpy of incompressible fluids and the ideal gas, respectively. These relations immediately yield Equ.(8.60) and Equ.(8.62) for the steady-state current of energy in heating of the fluid passing through the pipe in Fig. 8.9.

Mixing and entropy production in uniform flow systems. The application of the balance of entropy with the production rate applied to a flow heater requires some explanation. In the real situation, if we neglect fluid friction or other entropy producing processes, there is no dissipation in the fluid system. The fluid's temperature changes in the direction of flow from T_i to T_o. Entropy enters conductively from outside and if we treat the fluid as ideal (if it can be heated "easily"), there is no entropy production. Adding and removing entropy convectively at inlets and outlets is not dissipative either. So why do we have entropy production in the law of balance?

The reason is to be found in the form of the model. In contrast to the real situation where the temperature of the fluid is a function of position in the direction of flow, our model is one of uniform bodies. In the model in Fig. 8.9, or rather in the equations defining the model, it is assumed that the fluid has a single temperature T, which is the temperature at the outlet, $T = T_o$. In other words, there is a hot, well mixed fluid in the duct, and cold air is added to it at the inlet. The new air is immediately mixed with the hot air, and this is where entropy is produced.[7] Entropy production resulting from mixing will now be analyzed.

8.5.2 Filling a Hot Water Container: Mixing and Dissipation

Heat (entropy) storage systems for fluids such as water or gases are an important element of domestic and industrial thermal applications, and they play an important role in the heat budget of our planet. I will use the charging of storage elements to present the formulation of models of dynamical systems that include convective transfers. This serves to demonstrate the application of generalized dynamical laws of balance and proper constitutive relations, and we will be able to prove the relations for entropy production rates resulting from mixing of fluids on more general grounds.

Consider hot water (temperature T_f) flowing into a water tank as in Fig. 8.10; the flow rate is equal to I_m. There is already water present (mass m) that has a temperature T. Because of the inflow of fluid, the mass, entropy, and energy of the liquid in the control volume will increase. Since fluids at different temperatures are being mixed, there should be dissipation. We are interested in the temperature of the system as a function of time and in the rate of production of entropy. As far as the latter is concerned, we should be getting the same result as in Equ.(8.61) with the exception of the pressure term. To simplify matters a little, it is assumed that the pressure of the water entering

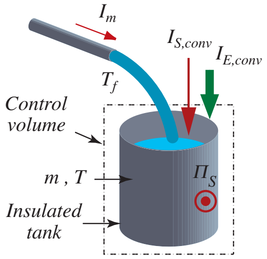


Figure 8.10: A liquid having temperature T_f flows into a tank with the same liquid at temperature T. The mass of liquid in the tank is m. Mass flow is I_m.

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[7] Since the production of entropy in a flow heater is a result of the type of model employed, it should vanish in a continuum model of the flow and heating of a fluid through a pipe. Indeed, if we divide the duct in Fig. 8.9 into several elements in the direction of flow, the total entropy production rate becomes smaller, the more elements there are. In the limit of many elements, the dissipation vanishes.

equals that of the water already in the tank, so we do not have entropy production due to friction as the pressure of the entering stream is relaxed. (Also, neglect pressure terms due to stacking of water in the gravitational field.)

Laws of balance. There are three laws of balance for the three fluidlike quantities that make up our model: mass, entropy, and energy:

$$\dot{m} = I_m \tag{8.65}$$

$$\dot{S} = I_{S,conv} + \Pi_S \tag{8.66}$$

$$\dot{E} = I_{E,conv} \tag{8.67}$$

Possible heat loss from the tank is neglected. Entropy and energy are extensive quantities, they scale with the amount of matter in the system: $S = ms$ and $E = me$ (Equ.(8.34)). Since the amount of fluid (its mass, its volume, etc.) is changing, we have to take the time derivatives of these products and obtain

$$m\dot{s} + s\dot{m} = I_{S,conv} + \Pi_S \tag{8.68}$$

$$m\dot{e} + e\dot{m} = I_{E,conv} \tag{8.69}$$

The constitutive laws for convective currents and for specific entropy and energy of incompressible media have been used before (Section 8.2.3 and Section 8.2.4). We solve Equ.(8.68) for the entropy production rate, replace *dm/dt* by I_m, use the GFF (Equ.(8.45)) to get *ds/dt* in terms of *de/dt*, then use Equ.(8.68) and insert the constitutive relations. This leads to

$$\begin{aligned}
\Pi_S &= m\dot{s} + s\dot{m} - I_{S,conv} \\
&= m\frac{1}{T}\dot{e} + c\ln\left(\frac{T}{T_{ref}}\right)\dot{m} - c\ln\left(\frac{T_f}{T_{ref}}\right)I_m \\
&= \frac{1}{T}\left(I_{E,conv} - e\dot{m}\right) + c\ln\left(\frac{T}{T_f}\right)I_m \\
&= \frac{1}{T}\left(c\left(T_f - T_{ref}\right)I_m - c\left(T - T_{ref}\right)\dot{m}\right) + c\ln\left(\frac{T}{T_f}\right)I_m
\end{aligned}$$

which finally turns into

$$\Pi_S = \left[\frac{1}{T}\left(T_f - T\right) - \ln\left(\frac{T_f}{T}\right)\right]cI_m \tag{8.70}$$

The result is equivalent to what was derived in Equ.(8.61) with the pressure term neglected.

8.5.3 Filling a Pressure Vessel With Hot Air

Here is a somewhat more sophisticated example of filling of a storage device, this time for a compressible fluid (Fig. 8.11). There is an amount *n* of (ideal) gas at temperature

T and pressure P present in the open system. Gas having a temperature T_f and a pressure P_f is entering at a rate I_n. We would like to know how the vessel responds to the inflow and how much entropy is produced in the mixing of the hot and cold air.

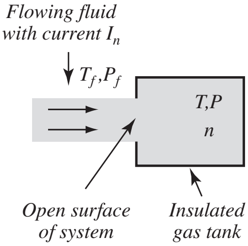


Figure 8.11: Ideal gas having temperature T_f and pressure P_f flows into a tank containing the same gas at temperature T and pressure P. The amount of substance of gas in the tank is n. the current of amount of substance is I_n.

The laws of balance needed here are those of amount of substance, entropy, and energy (again, mechanical effects will be neglected):

$$\dot{n} = I_n \tag{8.71}$$

$$\dot{S} = I_{S,conv} + \Pi_S \tag{8.72}$$

$$\dot{E} = I_{E,flow} \tag{8.73}$$

The expression for entropy is the same as that already written in Equ.(8.66), but the energy current in Equ.(8.73) is now the total current due to flow. With the flow energy current given by Equ.(8.19), we can evaluate the energy balance:

$$\dot{E} = \left(\bar{e}_f + P_f \bar{v}_f\right) I_n = \left(\bar{e}_f + RT_f\right) I_n$$

The second step is a consequence of the equations of state of the ideal gas (Section 5.2.3). Since the energy is the product of molar energy and amount of substance, the rate of change of energy is the derivative of this product. Therefore we have

$$\begin{aligned}
n\dot{\bar{e}} &= \left(\bar{e}_f + RT_f\right) I_n - \bar{e}\,\dot{n} \\
&= \left(\bar{e}_f - \bar{e} + RT_f\right) I_n \\
&= \bar{c}_V \left(T_f - T\right) I_n + RT_f I_n \\
&= \left(\bar{c}_p T_f - \bar{c}_V T\right) I_n
\end{aligned}$$

If we use the product rule on the rate of change of entropy of the system, the balance of entropy yields

$$\Pi_S = n\dot{\bar{s}} + \left(\bar{s} - \bar{s}_f\right) I_n$$

The first term on the right hand side is obtained from the Gibbs Fundamental Form for molar quantities, Equ.(8.35), and the difference of molar entropies is given by Equ.(8.12). If we also insert the result just derived for the rate of change of the molar energy, we have

$$\begin{aligned}
\Pi_S &= \frac{1}{T}\left[\left(\bar{c}_p T_f - \bar{c}_V T\right) I_n + nP\dot{\bar{v}}\right] + \left[-R\ln\left(\frac{P}{P_f}\right) + \bar{c}_p \ln\left(\frac{T}{T_f}\right)\right] I_n \\
&= \frac{1}{T}\left[\left(\bar{c}_p T_f - \left(\bar{c}_V + R\right)T\right) I_n + RT\,\dot{n} + nP\dot{\bar{v}}\right] \\
&\qquad + \left[-R\ln\left(\frac{P}{P_f}\right) + \bar{c}_p \ln\left(\frac{T}{T_f}\right)\right] I_n
\end{aligned}$$

Applying the equation of state of the ideal gas, and noting that the volume V of the system is constant, we can prove that

$$RT\,\dot{n} + nP\dot{\bar{v}} = 0$$

so the final result for the production rate of entropy is

$$\Pi_S = \frac{1}{T}\left(T_f - T\right)\bar{c}_p I_n + \left[-R\ln\left(\frac{P}{P_f}\right) + \bar{c}_p \ln\left(\frac{T}{T_f}\right)\right] I_n \tag{8.74}$$

This is equivalent to Equ.(8.63) which was derived for the example of a steady-state flow heater.

8.5.4 Experiment and Model of Mixing Hot and Cold Water

In Section 8.1, Fig. 8.1, an experiment of mixing of hot and cold water was presented. We are now in a position to construct a dynamical model for this application. I will simplify matters by de-coupling the hydraulic aspects from the thermal ones, and by using the measured temperature of the hot water in Tank 1 (Fig. 8.12, left). The decoupling of hydraulic processes is achieved by measuring rather than predicting the fluid currents occurring in the system. This leaves us with predicting the quantity and the temperature of the fluid in Tank 2.

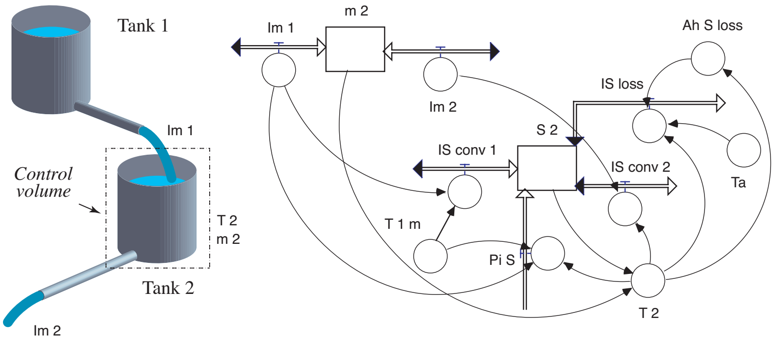


Figure 8.12: Mixing of hot water (Tank 1) with cold water (Tank 2). Right: Diagram of dynamical model for mass and temperature of the water in Tank 2.

The model (Fig. 8.12, right) is constructed using the balances of mass and entropy for Tank 2:

$$\frac{dm}{dt} = I_{m1} - I_{m2}$$

$$\frac{dS}{dt} = I_{S,conv1} - I_{S,conv2} - I_{S,loss} + \Pi_{S,mixing}$$

Remember that the mass fluxes are assumed to be known (they can be derived from measurements of the mass of water as functions of time). The convective entropy currents are obtained from

$$I_{S,conv} = c \ln\left(T/T_{ref}\right) I_m$$

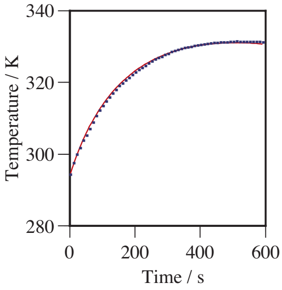


Figure 8.13: Data (dots) and simulation results (solid line) for temperature of water in the second tank of Fig. 8.12.

The temperature of the fluid is T_1—the temperature of the water in Tank 1—for the influx and T_2—the water temperature in Tank 2—for the outflow. This is because the liquid is stirred continuously in both tanks throughout the experiment.

The entropy production rate is calculated from Equ.(8.74) by setting $T_f = T_1$ and $T = T_2$. The entropy loss has been calculated with the help of Equ.(4.45) and Equ.(4.47). Here I have simplified matters greatly by including evaporative loss from Tank 2 with the conductive loss through the wall of the tin can. It turns our that the loss coefficient for conduction (calculated from surface area and overall transfer coefficient of the can) is about one third of the total to obtain satisfactory agreement between simulation and experimental results (Fig. 8.13).

8.5.5 Dynamical Model of a Solar Hot Water System

The following example combines a flow heater with hot water storage in a simple yet interesting technical system (see Fig. 8.14). Solar hot water heaters mainly consist of two components: a collector and a hot water storage tank. Naturally, there is more to it, but from a thermodynamics viewpoint, it makes sense to study this limited system.

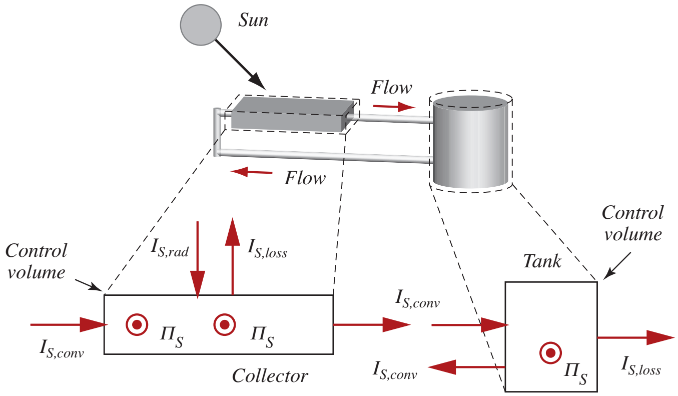


Figure 8.14: Top: A simple solar hot water system divided into two uniform bodies: the collector (absorber and liquid) and the storage tank. Bottom: Processes with respect to collector and tank.

The solar collector—the flow heater—consists of an absorber of solar radiation (a flat metal sheet), pipes that allow water or a water-glycol mixture to flow past the absorber so entropy can be collected, a glass cover to reduce entropy losses from the absorber to the environment, and insulation on the back, again to prevent heat loss. The phenomenon we are interested in from the perspective of flow systems is the heating of a (relatively) cool fluid as it passes along a hot plate (see Section 8.5.1). If we treat the absorber and the liquid present in the collector as a single body having a single temperature, there are six processes with respect to this body: (1) absorption of entropy and energy with radiation, (2) production of entropy due to absorption, (3 and 4) the convective flows of entropy at inlet and outlet, (5) entropy production due to mixing of the liquid flowing into the collector, and (6) entropy transfer to the environment through the glass cover (see Fig. 8.14).

The tank is an even simpler system if the water is mixed continuously (in reality, one wants to avoid mixing with its accompanying entropy production; without mixing, layers of different temperatures form in the tank leading to a fairly complex system to model). Hot water enters at one point, and the water having the temperature of the constantly mixed liquid flows out toward the collector at another point. Entropy is produced due to mixing of warm and cool water, and there is heat loss to the environment. Naturally, consumers will make use of the hot water during the day but this process is neglected in the model whose diagram is shown in Fig. 8.15.

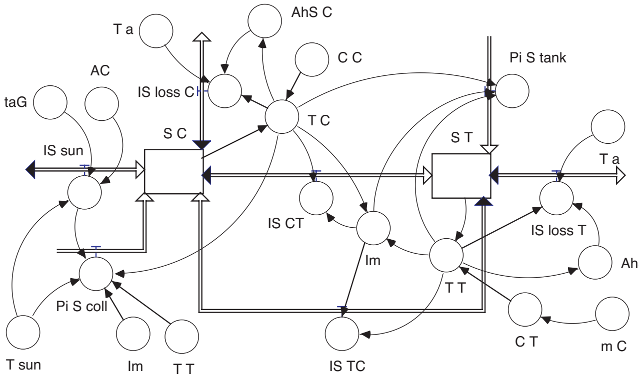


Figure 8.15: System dynamics diagram for a simple model of a solar hot water system. C stands for collector, and T denotes the tank. Note the expressions of laws of balance of entropy and associated processes that are discussed in the text.

Here are some of the more interesting constitutive expressions for the processes visible in the model diagram of Fig. 8.15. The entropy current coming in with solar radiation (or rather the part of it that is absorbed) is calculated as follows:

$$I_{S,sun} = \frac{4}{3}\frac{1}{T_{sun}} A_C(\tau\alpha)\mathcal{G} \tag{8.75}$$

(see Equ.(7.35) and Equ.(7.36)). T_{sun} is the surface temperature of the Sun, i.e., the temperature of solar radiation. A_c is the surface area of the collector, $\mathcal{G}$ is the irradiance at this surface, and $(\tau\alpha)$ is the fraction of radiation transmitted through the glass cover and absorbed by the collector (see Chapter 16 for more details).

The entropy production rate for the collector consists of two terms having to do with absorption of radiation and with mixing of the incoming fluid (the former takes the lions share):

$$\Pi_S = \left(\frac{3}{4}\frac{T_{sun}}{T_C} - 1\right) I_{S,sun} + cI_m\left[\frac{1}{T_C}(T_T - T_C) - \ln\left(\frac{T_T}{T_C}\right)\right] \tag{8.76}$$

where c is the specific heat of the liquid circulating in the system. The irreversibility in the tank is due to mixing. It is calculated as follows:

$$\Pi_S = cI_m\left[\frac{1}{T_T}(T_C - T_T) - \ln\left(\frac{T_C}{T_T}\right)\right] \tag{8.77}$$

Finally, we need to express the convective entropy currents. There are two independent ones related to the flow from the collector and from the tank:

$$
\begin{aligned}
I_{S,conv,CT} &= c I_m \ln\left(T_C / T_{ref}\right) \\
I_{S,conv,TC} &= c I_m \ln\left(T_T / T_{ref}\right)
\end{aligned}
\qquad \textbf{(8.78)}
$$

We have to make sure that the flow is turned on only if the temperature of the liquid in the collector is higher than the temperature in the tank.

The calculation of entropy losses is a standard one (see Chapter 7). A number of assumptions have been made to simplify the model. Chief among these are the model of a uniform collector (where all the components have the same temperature and the hotness does not vary in the flow direction), complete mixing of the liquid in the tank, no loss from pipes, and no energy consumption for pumping with its accompanying entropy production due to flow resistance. If we take a simple sinusoidal function for the daily irradiation $\mathcal{G}(t)$ (the same for every day which might happen for a sequence of clear days), and choose a constant value for the mass flux, the temperatures of collector and tank fluids might look like those shown in Fig. 8.16.

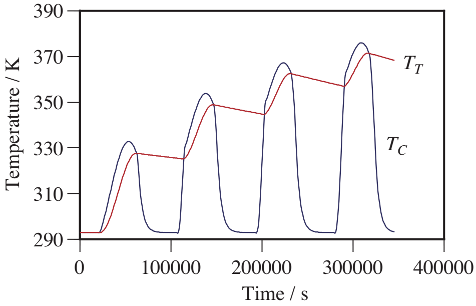


Figure 8.16: System dynamics diagram for a simple model of a solar hot water system. C stands for collector, and T denotes the tank. Note the expressions of laws of balance of entropy and associated processes that are discussed in the text.

Models of this type can be used to design solar heating systems. Playing with the parameters of the system can give us a feeling for adequate sizing. Moreover, if we quantify entropy production, we have a means of designing for minimal irreversibility, a subject we are going to take up in Chapter 9.

QUESTIONS

13. If air (or water) flows through a flow heater without mixing and without friction, why is the process reversible? (Take only the fluid in the heater as the system.) Why did we get a non-zero entropy production rate in our analysis of the flow heater? (See Fig. 8.9 and Equ.(8.61) or Equ.(8.63).)
14. Why is the pressure term present in Equ.(8.61) missing from Equ.(8.70)?
15. When an incompressible fluid is mixed with one already present, and if the pressure of the former is higher than that of the latter, there is dissipation due to the pressure effect. Why? Is the term that applies to the mixing of air visible in the equation? (Equ.(8.74))
16. How could the system shown in Fig. 8.10 be changed if we want to include the effect of pressure differences (upon entropy production) between incoming and stored fluid?
17. Why does the daily rise of temperature of water in the solar tank of Fig. 8.14 (see graph in Fig. 8.16) get smaller day after day? (The irradiation is the same every day.)

18. If water in the storage tank of a solar hot water system is constantly mixed, there is entropy production due to this mixing. Clearly, mixing does not alter the energy of the system, so there is no apparent "energy loss" due to this effect. Still, one tries to avoid mixing in solar tanks. Why is a system with a layered tank (hot water on top of cooler water) more efficient? Where does the loss due to entropy production become apparent?

EXAMPLE 8.6. The temperature of glycol in a tank with an inflow of hot glycol.

Imagine glycol having temperature T_f flowing into a tank also containing glycol at a temperature T (the present mass of glycol is m, and the mass flux is I_m). Assume the tank to be perfectly insulated. Remember that glycol is a fluid having constant entropy capacitance (Fig. 4.37). (a) Determine the specific energy of glycol as a function of temperature. (b) Derive the entropy production rate as a result of mixing of glycol at different temperatures. (c) Derive the differential equation for the temperature of glycol in the tank and solve it.

SOLUTION: (a) The energy of glycol can be calculated with the help of the Gibbs Fundamental Form for incompressible fluids

$$\dot{e} = T\,\dot{s}$$

which follows from Equ.(8.35). Since glycol has a constant (specific) entropy capacitance k, integration of this form leads to

$$e - e_{ref} = \int_0^t T\,\dot{s}\,dt = \int_0^t T\,k\dot{T}\,dt = k\int_{T_{ref}}^{T} T\,dT = \frac{1}{2}k\left(T^2 - T_{ref}^2\right)$$

(b) The derivation of the entropy production rate proceeds along the same lines that led to Equ.(8.70) (Section 8.5.2). The laws of balance of entropy and of mass, the GFF, and the constitutive expression for the convective current and the specific entropy lead to

$$\begin{aligned} \Pi_S &= m\dot{s} + s\dot{m} - s_f I_m \\ &= m\frac{1}{T}\dot{e} + \left(s - s_f\right)I_m = m\frac{1}{T}\dot{e} + k\left(T - T_f\right)I_m \end{aligned}$$

With the help of the law of balance of energy we find that

$$m\dot{e} = \left(e_f - e\right)I_m = \frac{1}{2}k\left(T_f^2 - T^2\right)I_m$$

This leads to the final expression for the entropy production rate due to mixing of a stream of glycol with glycol in a tank:

$$\Pi_S = \left[\frac{1}{2}\frac{1}{T}\left(T_f^2 - T^2\right) + \left(T - T_f\right)\right]kI_m$$

(c) We can use the law of balance of entropy and appropriate constitutive relations to derive the differential equation for the temperature of the liquid in the tank:

$$\begin{aligned} m\dot{s} &= s_f I_m - s\dot{m} + \Pi_S \\ mk\dot{T} &= k\left(T_f - T\right)\dot{m} + \left[\frac{1}{2}\frac{1}{T}\left(T_f^2 - T^2\right) + \left(T - T_f\right)\right]k\dot{m} \end{aligned}$$

which leads to

$$mk\dot{T} = \frac{1}{2}\frac{1}{T}\left(T_f^2 - T^2\right)k\dot{m}$$

This is a separable differential equation for the variables T and m:

$$\frac{2T}{T_f^2 - T^2}\frac{dT}{dt} = \frac{1}{m}\frac{dm}{dt} \quad \Rightarrow \quad \int_{T_0}^{T}\frac{2T}{T_f^2 - T^2}dT = \int_{m_0}^{m}\frac{1}{m}dT$$

The index 0 refers to the initial state. Integrating leads to

$$-2\cdot\frac{1}{2}\ln\left(\frac{T_f^2 - T^2}{T_f^2 - T_0^2}\right) = \ln\left(\frac{m}{m_0}\right) \quad \Rightarrow \quad T^2 = T_f^2 - \left(T_f^2 - T_0^2\right)\frac{m_0}{m}$$

The temperature of the incoming fluid is attained in the limit of a large amount of added glycol.

EXAMPLE 8.7. Isothermal incompressible fluid flow with friction.

As in the case of Bernoulli's law (Example 8.3), consider the steady-state isothermal flow of an incompressible fluid through a pipe. Include the effect of friction and derive an expression for the rate of production of entropy in terms of the pressures and the speeds involved. Use a formulation that involves the chemical potential of the fluid.

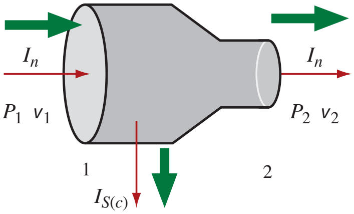


Figure Ex.7

SOLUTION: A control volume analysis is performed on the system displayed in Fig. Ex.7 (see also the figure of Example 8.3). In addition to the currents associated with the flow at points 1 and 2, there are fluxes of entropy and energy due to the cooling of the fluid. Since entropy is produced and the temperature of the incompressible fluid is assumed to be constant, entropy has to be emitted. The law of balance of entropy therefore reads

$$\Pi_S = -\left(I_{S,conv,1} + I_{S,conv,2} + I_{S(c)}\right)$$

The contribution of the convective currents cancels out since the specific entropy of the isothermal incompressible fluid remains constant if the temperature is constant. Therefore, the entropy current due to cooling is equal to the rate of production of entropy.

The equation of balance of energy includes the currents due to fluid flow and to cooling. They can be written as

$$\mu_1 I_{n1} + T I_{S,conv,1} + v I_{p,conv,1} + \mu_2 I_{n2} + T I_{S,conv,2} + v I_{p,conv,2} + T I_{S(c)} = 0$$

With the general expression for the chemical potential of the fluid (Equ.(8.43)), we obtain the following result

$$M_0\left[\left(\frac{P_1}{\rho}+\frac{1}{2}v_1^2\right)-\left(\frac{P_2}{\rho}+\frac{1}{2}v_2^2\right)\right]I_{n1}+TI_{s(c)}=0$$

which can be transformed into

$$\Pi_S=\left[\left(\frac{P_1}{\rho}+\frac{1}{2}v_1^2\right)-\left(\frac{P_2}{\rho}+\frac{1}{2}v_2^2\right)\right]\frac{|I_m|}{T}$$

In contrast to the case of ideal flow, the sum of the pressure term and the velocity term is not constant along the fluid stream.

EXAMPLE 8.8. Charging a hot water tank.

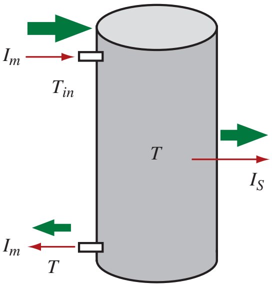


Figure Ex.8

A tank containing 1000 liters of water at 20°C is charged with a stream of hot water at 60°C while the same amount of water is withdrawn from an outlet (see Fig. Ex.8). The mass flux is set equal to 0.05 kg/s. The water supplied to the tank instantaneously mixes with the fluid already there. There is heat loss to the surroundings at ambient temperature of 20°C; the heat loss coefficient-surface area product is 10 W/K. (a) Calculate the temperature of the water in the tank as a function of time. (b) Which parameters does the maximum temperature reached in the tank depend upon? (c) Calculate the rate of production of entropy.

SOLUTION: (a) The law of balance of energy yields the differential equation for the temperature of the water as a function of time:

$$\dot{E}=I_{E,flow,1}+I_{E,flow,2}+I_{E,loss}$$

The terms in this equation can be expressed using the constitutive relations derived so far:

$$C\dot{T}=c|I_m|(T_{in}-T)-UA(T-T_a)$$

C is the temperature coefficient of energy of the water in the tank, and U denotes the (heat) transfer coefficient from the tank to the environment. The differential equation can be integrated directly:

$$C\int_{T_{init}}^{T}\frac{dT}{a-bT}=t$$
$$a=c|I_m|T_{in}+UAT_a$$
$$b=c|I_m|+UA$$

which leads to

$$T(t)=\frac{a}{b}-\left(\frac{a}{b}-T_{init}\right)\exp\left(-\frac{b}{C}t\right)$$

(b) The maximum temperature reached by the fluid inside the tank is equal to

$$T_{max}=\frac{a}{b}=\frac{c|I_m|T_{in}+UAT_a}{c|I_m|+UA}$$

Increasing the loss factor *UA* decreases the maximum possible temperature. If there is no heat loss, the maximum temperature is the temperature of the water supplied to the tank.

(c) The equation of balance of entropy for the control volume coinciding with the water in the tank is

$$\dot{S} - c_p\left|I_m\right|\ln\left(\frac{T_{in}}{T}\right) + \frac{UA\left(T - T_a\right)}{T} = \Pi_S$$

Since the rate of change of the entropy of the incompressible body of water is related to the rate of change of its energy by the Gibbs fundamental form, we obtain

$$\Pi_S = \frac{1}{T}c_p\left|I_m\right|\left(T_{in} - T\right) - c_p\left|I_m\right|\ln\left(\frac{T_{in}}{T}\right)$$

Performing a balance of entropy on flow systems is as important as it is for other processes. Take the example of a hot water tank hooked up to solar collectors. If the water is stratified according to temperature (warmer water at the top), rather than mixed, the efficiency of the system will be higher. Naturally, with stratification, the amount of entropy produced, and therefore the magnitude of the irreversibility of the process, is smaller than with mixing.

EXAMPLE 8.9. Analysis of a parabolic trough solar power plant.

Analyze some aspects of the operation of a solar thermal power plant that uses parabolic trough mirrors to heat oil. The oil is used to produce steam to drive a heat engine.

Data and assumptions. Irradiance: 1000 W/m^2, concentration factor for solar radiation: 40; length of pipe carrying oil: 100 m, radius: 5.0 cm; specific heat of oil: 2000 J/(K·kg); ambient temperature: 20°C. Assume the surfaces of the pipe to be perfect absorbers and emitters of radiation. Convective heat transfer coefficient from pipe to air: 15 W/(K·m^2). Assume the pipe material to be a perfect conductor for heat. The oil leaves the pipe in the parabolic trough at T_H = 350°C. It is cooled in the power plant to T_L = 300°C and returned to the pipe.

(a) Assume the pipe to be made of a single (thin) shell of glass. Construct a single body steady-state model of the oil. Determine the rate of absorption of energy from radiation. Determine the energy currents due to convective and radiative loss at the surface of the pipe. Use this to calculate the (mass) flux of oil needed to satisfy the balance of energy in steady-sate. Determine the ratio of losses to solar gain. What happens if the (direct) irradiance is reduced to 700 W/m^2? (b) Losses turn out to be a very high fraction in the model in (a). For this reason, assume the pipe to have a second shell around the inner (oil carrying) pipe. Assume there is perfect vacuum between the cylindrical shells. Create the new steady-state model and repeat the calculations of problem (a). (c) A heat engine receives entropy from the oil from 100 parallel troughs. What is the entropy current due to cooling of the oil?

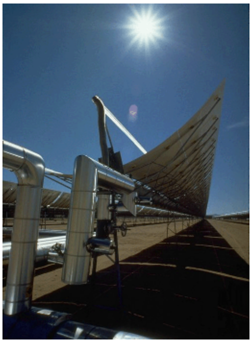


Figure Ex.9

SOLUTION: (a) Assuming the pipe material to be a perfect conductor means that it will have the same temperature as the oil and therefore does not have to be treated as a separate body. To find the energy of radiation absorbed by the pipe (or rather, by the oil), assume that the Sun's light is concentrated onto half of the circumference of the circular pipe:

$$\Sigma_E = \pi r L c \mathcal{G} = \pi\cdot 0.050\cdot 100\cdot 40\cdot 1000\,\mathrm{W} = 628\,\mathrm{kW}$$

Let us assume that the temperature of the oil is an average 325°C = 598 K. Losses occur over the entire surface of the pipe and are therefore equal to

$$\begin{aligned} I_{E,loss} &= 2\pi r L h_{loss}\left(T_{av} - T_a\right) + 2\pi r L \sigma\left(T_{av}^4 - T_a^4\right) \\ &= 2\pi\cdot 0.050\cdot 100\cdot\left(15\cdot\left(598 - 293\right) + 5.67\cdot 10^{-8}\left(598^4 - 293^4\right)\right)\mathrm{W} = 358\,\mathrm{kW} \end{aligned}$$

The balance of energy allows us to calculate the mass flux of oil through the pipe:

$$
\begin{aligned}
& cI_m\left(T_{\mathrm{H}}-T_{\mathrm{L}}\right)=\Sigma_E-I_{E,\,loss} \\
& I_m=\frac{\Sigma_E-I_{E,\,loss}}{c\left(T_{\mathrm{H}}-T_{\mathrm{L}}\right)}=\frac{628-358}{2000\cdot(350-300)}\cdot 10^3\,\frac{\mathrm{kg}}{\mathrm{s}}=2.7\,\frac{\mathrm{kg}}{\mathrm{s}}
\end{aligned}
$$

Losses are about 57% of solar gain. If the insolation drops to 700 W/m^2, the losses amount to about 81%.

(b) There are now two bodies to be considered, the pipe with its oil and the surrounding shell. Assume the shell to be transparent for solar light but opaque for the radiation coming from the hot inner pipe. Now the laws of balance of energy for the pipe and shell are

$$
\begin{aligned}
& cI_m\left(T_{\mathrm{H}}-T_{\mathrm{L}}\right)=\pi rLc\,\mathcal{G}-2\pi rL\sigma\left(T_{av}^4-T_{shell}^4\right) \\
& 2\pi rL\sigma\left(T_{av}^4-T_{shell}^4\right)=2\pi rLh_{loss}\left(T_{shell}-T_a\right)+2\pi r_{shell}L\sigma\left(T_{shell}^4-T_a^4\right)
\end{aligned}
$$

Again, the temperature of the pipe is taken to be the average of inlet and outlet temperatures of the oil, and the shell is assumed to take a single temperature T_{shell}. For T_{av} = 598 K, the fraction of losses drops to 23% and the temperature of the shell is 462 K (189°C). The mass flux of oil needed to keep the operation at steady-state increases to 4.8 kg/s.

(c) The oil is cooled in the engine from 350°C down to 300°C. The current of the 100 parallel troughs is 480 kg/s. In steady-state, the balance of entropy leads to

$$
I_{S,conv,net}=cI_m\ln\left(\frac{T_{\mathrm{H}}}{T_{\mathrm{L}}}\right)=2000\cdot 480\cdot\ln\left(\frac{350+273}{300+273}\right)\frac{\mathrm{W}}{\mathrm{K}}=80\,\frac{\mathrm{kW}}{\mathrm{K}}
$$

A completely reversible Carnot engine running between 325°C and 20°C would therefore have a power of roughly 300 K · 80 kW/K = 2400 kW. A real engine might achieve half of this which would translate into a thermal efficiency (solar to electric) of about 20%. This very rough estimate agrees very well with the actual data that gives typical values of up to 25%.

8.6 FLUID FLOW WITHOUT HEATING OR COOLING

In this section, we will discuss examples where the flow is thermally isolated, namely isentropic flow of the ideal gas, the throttling process, and the flow through a reactor of a fuel undergoing combustion without losing heat to its surroundings. The first process might model a rocket engine, while the second occurs in refrigeration systems using vapor compression, and in processes for liquefying gases. The third example will lead to the notion of adiabatic flame temperature. We have already discussed one example of the type treated here: if the fluid is incompressible and the flow isentropic, we have the case for which Bernoulli's law applies.

8.6.1 Steady State Equations of Balance

Independent of what happens inside the pipe, as long as there is no exchange of energy through the walls channelling the flow, the only energy currents are the result of fluid flow at positions 1 and 2 (Fig. 8.17). The equation of balance of energy therefore takes the form

$$
\left[\mu_1+T_1\bar{s}_1+M_0v_1^2\right]I_{n1}+\left[\mu_2+T_2\bar{s}_2+M_0v_2^2\right]I_{n2}=0 \tag{8.79}
$$

Since the fluxes of amount of substance are of the same magnitude at the inlet and the outlet, this is equivalent to

$$\mu_1 + T_1 \bar{s}_1 + M_0 v_1^2 = \mu_2 + T_2 \bar{s}_2 + M_0 v_2^2 \tag{8.80}$$

If we use Equ.(8.43) for the chemical potential of the fluid, we obtain

$$\bar{h}_2 - \bar{h}_1 = -\frac{1}{2} M_0 \left[v_2^2 - v_1^2 \right] \tag{8.81}$$

In applications, the state of the fluid at the inlet of the pipe might be specified, and we may wish to compute the quantities at the outlet. The equation of balance of energy does not generally suffice for getting the required answer. We therefore have to be more specific about the details of the flow, and apply the other laws of balance as well. The balance of entropy simply states that

$$\bar{s}_1 I_{n1} + \bar{s}_2 I_{n2} = -\Pi_S \tag{8.82}$$

The balance of momentum must be applied if information about forces upon sections of the fluid (or the pipes) is desired; it will not be considered at this point.

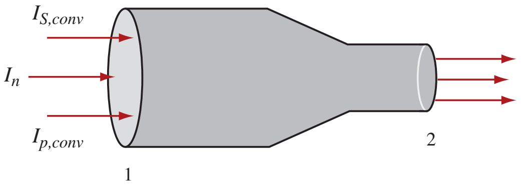


Figure 8.17: Assume that the fluid flowing through the pipe does not exchange any heat with the walls. As a consequence, the energy currents are only due to fluid flow.

8.6.2 Isentropic Flow of the Ideal Gas

In the case of the ideal gas we have the necessary constitutive information for computing what happens to the fluid. Equ.(8.81) becomes

$$\bar{c}_p \left(T_1 - T_{ref} \right) + \frac{1}{2} M_0 v_1^2 = \bar{c}_p \left(T_2 - T_{ref} \right) + \frac{1}{2} M_0 v_2^2 \tag{8.83}$$

(see Equ.(8.53)). This shows that the temperature of the fluid decreases with increasing speed of flow. However, we are not able to calculate the state at the outlet from this information and the specification of the state at the inlet. We need the equations of balance of amount of substance (or mass) and of entropy:

$$\left| I_{n1} \right| = \left| I_{n2} \right| \quad \Rightarrow \quad \rho_1 A_1 v_1 = \rho_2 A_2 v_2 \quad \Rightarrow \quad \frac{P_1}{T_1} A_1 v_1 = \frac{P_2}{T_2} A_2 v_2 \tag{8.84}$$

$$\left| I_{S,conv,1} \right| = \left| I_{S,conv,2} \right| \quad \Rightarrow \quad \bar{s}_1 = \bar{s}_2 \quad \Rightarrow \quad -R \ln\left(\frac{P_2}{P_1} \right) + \bar{c}_p \ln\left(\frac{T_2}{T_1} \right) = 0 \tag{8.85}$$

Remember that the flow was assumed to be isentropic; in other words, it must be reversible. The last forms hold for the ideal gas with a constant temperature coefficient of enthalpy (Equ.(8.52)). Note that Equ.(8.85) leads to the well-known formula for adiabatic changes of the ideal gas which was derived in Chapter 5.

8.6.3 The Throttling Process

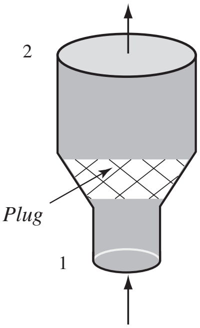


Figure 8.18: A gas is allowed to expand through a porous plug. If the fluid is near the point of condensation, the reduction in pressure can lead to a decrease of temperature.

In the throttling process, a fluid is allowed to flow through some sort of valve or porous plug which reduces its pressure. If the valve is insulated, it will not lead to an exchange of energy and entropy with the surroundings, leaving our main assumption valid. If the diameter of the pipe is changed so as to leave the speed of flow unchanged upon expansion of the fluid, the expression of the balance of energy reduces to

$$\bar{h}_2 = \bar{h}_1 \tag{8.86}$$

The laws of balance for amount of substance and entropy take the forms

$$\frac{A_1}{\bar{v}_1} = \frac{A_2}{\bar{v}_2} \tag{8.87}$$

and

$$\Pi_S = -\left(\bar{s}_1 I_{n1} + \bar{s}_2 I_{n2}\right) \tag{8.88}$$

respectively. Clearly, the flow is irreversible, i.e., entropy is produced. Note that for the ideal gas, the condition of constant enthalpy requires the temperature to remain constant: ideal gases do not change their temperature as a result of throttling, and they cannot be liquefied. For other gases, property data have to be known for the chemical potential, entropy, energy, enthalpy, and specific volume.

8.6.4 Adiabatic Mixing of Streams of Non-Reacting Ideal Gases

A generalization of the previous discussion leads to a practically relevant situation. Gases are mixed dynamically when streams of different substances come together to form a new mixture. In the following, steady-state adiabatic mixing of two streams of different non-reacting ideal gases will be treated (see Fig. 8.19).

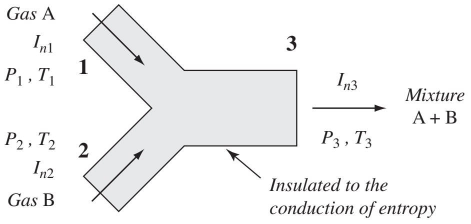


Figure 8.19: Streams of different gases A and B are mixed inside an well insulated reactor and then exit at point 3.

The situation is governed by three laws of balance, namely those for amount of substance, entropy, and energy. Details are determined by the properties of the gases at the inlets and the outlet. If some of the conditions—flows, pressures, and temperatures—are given, missing quantities can be calculated.

Laws of balance. There are three flows at the two inlets and the single outlet defined in Fig. 8.19, and each of them represents a bundle of flows of quantities. The steady-state balance of amount of substance takes the form

$$I_{n1} + I_{n2} = I_{n3} \tag{8.89}$$

Since the gases do not react, the substance A and B are still present in the original amounts in stream 3:

$$I_{n3} = I_{nA} + I_{nB} \tag{8.90}$$

The law of balance of entropy contains four terms: three convective flows and the production rate:

$$\bar{s}_{1A} I_{n1} + \bar{s}_{2B} I_{n2} + \Pi_S = \bar{s}_{3(A+B)} I_{n3} \tag{8.91}$$

Dissipation is due to mixing, temperature changes, and pressure changes. On the right hand side, the average entropy of the mixture appears. According to the mixing rules of non-interacting gases (Section 6.6.3) and the balance of amount of substance, the right hand side can be written as follows:

$$\bar{s}_{3(A+B)} I_{n3} = \bar{s}_{3A} I_{n1} + \bar{s}_{3B} I_{n2} \tag{8.92}$$

The law of balance of energy only involves the convective currents of energy at the three openings of the reactor in Fig. 8.19. According to what we derived above, the convective energy current at each of the inlets and outlets equals the product of molar enthalpy and current of amount of substance (if effects of speed and height in the gravitational field are neglected):

$$\bar{h}_{1A} I_{n1} + \bar{h}_{2B} I_{n2} = \bar{h}_{3(A+B)} I_{n3} \tag{8.93}$$

As in the case of entropy shown above in Equ.(8.92), the right hand side can be written as follows:

$$\bar{h}_{3(A+B)} I_{n3} = \bar{h}_{3A} I_{n1} + \bar{h}_{3B} I_{n2} \tag{8.94}$$

Entropies and enthalpies. Now we apply the property rules for ideal gases to the substances at points 1, 2, and 3. If we introduce reference values T_{ref} and P_{ref} for temperature and pressure and set entropy and enthalpy equal to zero at the reference points, we obtain:

$$\begin{aligned}
\bar{s}_{1A}(P_1, T_1) &= -R \ln\left(P_1/P_{ref}\right) + c_{PA} \ln\left(T_1/T_{ref}\right) \\
\bar{s}_{2B}(P_2, T_2) &= -R \ln\left(P_2/P_{ref}\right) + c_{PB} \ln\left(T_2/T_{ref}\right) \\
\bar{s}_{3A}(P_{3A}, T_3) &= -R \ln\left(P_{3A}/P_{ref}\right) + c_{PA} \ln\left(T_3/T_{ref}\right) \\
\bar{s}_{3B}(P_{3B}, T_3) &= -R \ln\left(P_{3B}/P_{ref}\right) + c_{PB} \ln\left(T_3/T_{ref}\right)
\end{aligned} \tag{8.95}$$

The enthalpies are calculated for the same four conditions. Remember that the enthalpy of the ideal gas depends only on temperature:

$$\begin{aligned}
\bar{h}_{1\mathrm{A}}\left(P_1,T_1\right) &= c_{P\mathrm{A}}\left(T_1 - T_{ref}\right)\\
\bar{h}_{2\mathrm{B}}\left(P_2,T_2\right) &= c_{P\mathrm{B}}\left(T_2 - T_{ref}\right)\\
\bar{h}_{3\mathrm{A}}\left(P_{3\mathrm{A}},T_3\right) &= c_{P\mathrm{A}}\left(T_3 - T_{ref}\right)\\
\bar{h}_{3\mathrm{B}}\left(P_{3\mathrm{B}},T_3\right) &= c_{P\mathrm{B}}\left(T_3 - T_{ref}\right)
\end{aligned} \tag{8.96}$$

These rules for entropy and enthalpy apply to the model of the ideal gases having constant temperature coefficients of enthalpy c_P. Note that the pressures of gases A and B at the exit (point 3), $P_{3\mathrm{A}}$ and $P_{3\mathrm{B}}$, are the partial pressures of the respective components in the mixture.

Partial pressures. The partial pressures of components A and B can be calculated from the relative amounts of A and B. With

$$\bar{x}_{\mathrm{A}} = \frac{I_{n\mathrm{A}}}{I_{n\mathrm{A}} + I_{n\mathrm{B}}} \quad , \quad \bar{x}_{\mathrm{B}} = \frac{I_{n\mathrm{B}}}{I_{n\mathrm{A}} + I_{n\mathrm{B}}} \tag{8.97}$$

the partial pressures are

$$P_{3\mathrm{A}} = \bar{x}_{\mathrm{A}} P_3 \quad , \quad P_{3\mathrm{B}} = \bar{x}_{\mathrm{B}} P_3 \tag{8.98}$$

8.6.5 Flow With Combustion: Adiabatic Flame Temperature

How hot is the flame of burning fuel? The temperature is determined by three factors: first, by the amount of entropy produced by the reaction; second, by how much entropy is retained by the combustion products; and, finally, by the temperature dependence of the entropy of the substances involved in the reaction and in the flow through the reactor. If you let the reaction take place at constant pressure, the rise in temperature certainly cannot be the result of compression. Rather, the temperature of the combustion products depends directly upon how much entropy they contain.

Consider a simple flow reactor (Fig. 8.20) with reactants entering at standard conditions, and products of the reaction leaving at an unknown temperature T. The value of T will be highest if there is no entropy lost to the surroundings: this is the condition to which the name *adiabatic flame temperature* applies. Our steady-state analysis will begin with the balance of entropy. The entropy leaving convectively with the products of the reaction must be the entropy produced during combustion, plus the entropy supplied by the reactants, i.e., by the fuel and the oxidizer:

$$\left|I_{S,conv,out}\right| = \Pi_S + \left|I_{S,conv,in}\right| \tag{8.99}$$

During adiabatic operation, there will be no other entropy flux to or from the surroundings. The quantity which determines the entire outcome is the amount of entropy produced, which is governed by the magnitude of dissipation, which in turn depends upon whether or not other processes are involved. Since the substances burn at a different temperature from that of the entering fluid stream, there is indeed something else happening: the entropy entering the reactor with the reactants is lifted from temperature T_0 to a final value of T. Hence, the energy released by the combustion is divided among two processes. Fig. 6.30 gives the rate at which energy is released; the expressions for the energy dissipated, and for the energy used in lifting an amount of energy, are well known. Therefore, the balance of power reads:

$$\frac{1}{\nu_i}\left[\Delta\mu\right]_{Reaction}\Pi_{n,i} = T\,\Pi_S + \left(T - T_0\right)\left|I_{S,conv,in}\right| \tag{8.100}$$

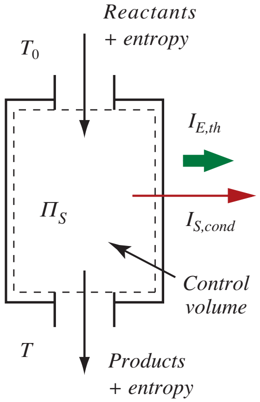


Figure 8.20: Fuel and oxidizer are burned in a flow reactor. If there is no loss of entropy to the surroundings, the process is adiabatic, and the temperature of the products is the adiabatic flame temperature.

ν_i is the stoichiometric coefficient of the *i*-th term in the reaction equation (Fig. 8.101 below). All three terms contain the unknown temperature of the combustion products. If we manage to properly express all the quantities in the previous two equations, we can solve the expressions—which are normally nonlinear—for T. First, the change of the chemical potential for the reaction is computed in the following manner. Write the reaction equation as follows:

$$fuel + \nu_2 oxidizer + \nu_3 \mathrm{A} + \ldots = \nu_4 \mathrm{C} + \nu_5 \mathrm{D} + \ldots \tag{8.101}$$

Note that the stoichiometric coefficient multiplying the fuel has been set equal to one, i.e., $\nu_1 = 1$. On the left, we have the reactants, which may include substances which do not necessarily take part in the combustion. This is the case, for example, if a fuel is mixed with air, containing mostly nitrogen. If we set $i = 1$, the power of the chemical reaction takes the form

$$\begin{aligned}&\left[\Delta\mu\right]_{Reaction}\Pi_{n,fuel} = \\ &\left|\Pi_{n,fuel}\right|\left\{\sum_{reactants}\nu_i\left[\bar{h}_i(T_0) - T_0\bar{s}_i(T_0)\right] - \sum_{products}\nu_j\left[\bar{h}_j(T) - T\,\bar{s}_j(T)\right]\right\}\end{aligned} \tag{8.102}$$

(see Equ.(8.48)). $\Pi_{n,fuel}$ is the rate at which fuel is burned in the reactor (remember that the chemical potential difference and the consumption rate are both negative). Next, the convective entropy currents have to be written down for the particular chemical constituents of the fluids, and for the particular physical conditions:

$$\begin{aligned}\left|I_{s,conv,in}\right| &= \left|\Pi_{n,fuel}\right|\sum_{reactants}\nu_i\bar{s}_i(T_0)\\ \left|I_{s,conv,out}\right| &= \left|\Pi_{n,fuel}\right|\sum_{products}\nu_j\bar{s}_j(T)\end{aligned} \tag{8.103}$$

Here, it is assumed that the fuel is completely consumed so that the rate of fuel consumption must be equal to the flow of fuel. Combining the different parts, we arrive at the following expression for the rate of production of entropy:

$$\Pi_S = \frac{\left|\Pi_{n,fuel}\right|}{T}\left\{\sum_{reactants}\nu_i\left[\bar{h}_i(T_0) - T\,\bar{s}_i(T_0)\right] - \sum_{products}\nu_j\left[\bar{h}_j(T) - T\,\bar{s}_j(T)\right]\right\} \tag{8.104}$$

Note that in the first term on the right, the exit temperature T appears as a factor of $s_i(T_0)$ (and not T_0). These equations tell us that we must know the entropy and the enthalpy of reactants and products at their respective temperatures (and at constant pressure), with the temperature of the products still unknown, if we want to do the calculations. One way of doing this is by approximating the dependence of enthalpy and entropy upon temperature using average temperature coefficients of enthalpy c_P

for the species. (Such values may be read off the graph in Fig. 5.14 of Chapter 5). The nonlinear equations can be solved iteratively.

Apart from the fuel and the oxidizer, there might be several other substances involved in the flow through the reactor, as in the case of fuel mixed with air. Also, we might use too much of the oxidizer or of the air, or too little; in the latter case some of the fuel will not be burned. In either case, all these factors negatively influence the outcome of the combustion process compared to the case of a mixture of fuel and the right amount of the oxidizer (and nothing else). The amount of air delivering the proper mass of oxygen for complete combustion of the fuel is called the *theoretical amount of air*.

EXAMPLE 8.10. Temperature reduction in steam as a result of throttling.

Use the following steam table (Table 8.1) to estimate the reduction of the temperature resulting from the irreversible expansion of steam. The diameter of the pipe is increased so that the pressure of the steam is reduced from 1.0 bar to 0.70 bar. Initially, the steam is at a temperature of 120°C. Also calculate the new specific volume and the necessary change of the diameter of the pipe. Finally, compute the entropy produced per kilogram of steam passing through the porous plug in the throttling device.

SOLUTION: According to the balance of energy, the enthalpy of the fluid must remain constant as a result of the process. The specific enthalpy at the inlet is $h(P{=}1.0, T{=}120) = 2716.6$ kJ/kg. Finding this same value in the table for a pressure of 0.70 bar yields a temperature of $T_2 = 118.3$°C by linear interpolation between the appropriate values.

Table 8.1: A small portion of the steam tables

P / bar	***T*** / °C	υ / m^3/kg	***e*** / kJ/kg	***h*** / kJ/kg	***s*** / kJ/(K·kg)
0.70	100	2.434	2509.7	2680.0	7.534
	120	2.571	2539.7	2719.6	7.638
	160	2.841	2599.4	2798.2	7.828
1.0	100	1.696	2506.7	2676.2	7.361
	120	1.793	2537.3	2716.6	7.467
	160	1.984	2597.8	2796.2	7.660

We use this new temperature to interpolate to find the specific volume and the specific entropy of the fluid: $\upsilon_2 = 2.559$ m^3/kg and $s_2 = 7.629$ kJ/(K·kg).

With a value of υ_1=1.793 m^3/kg at the inlet, we can infer that the cross section of the pipe has to increase by a factor of 1.427, which means that the radius at the outlet must be larger than at the inlet by a factor of 1.195.

The specific entropy at the inlet is 7.467 kJ/(K·kg). Therefore, the amount of entropy produced is 162 J/(K·kg).

EXAMPLE 8.11. Burning methane with oxygen and with different amounts of air.

(a) Let methane burn completely with oxygen. Determine the adiabatic flame temperature for this reaction. (b) Calculate the theoretical amount of air for the combustion of methane. Assume air to be composed of nitrogen and oxygen. (c) Determine the adiabatic flame temperature for the theoretical amount of air. (d) Vary the amount of air (both up and down) and compute both the flame temperature and the rate of production of entropy (per unit amount of methane). (e) Demonstrate that Equ.(8.104) and the balance of entropy lead to the expression

$$\sum_{reactants} v_i \bar{h}_i(T_0) = \sum_{products} v_j \bar{h}_j(T)$$

The enthalpy of the entering mixture is equal to the enthalpy of the fluid stream exiting the reactor.

Table 8.2: Molar enthalpy and entropy of substances involved in combustion[a]

T / K	*h*_CH4	*h*_O2	*h*_CO2	*h*_H2O	*s*_CH4	*s*_O2	*s*_CO2	*s*_H2O
298	–74870	0	–393520	–241820	186	205	214	189
1000	–36686	22705	–360161	–215795	248	243	269	233
2000	48678	59197	–302123	–169166	306	269	309	264
3000	145200	98084	–240730	–115419	345	284	334	286
4000	238396	139013	–177782	–58825	372	296	352	302
5000	320356	182045	–112279	–2589	390	306	367	315
6000	386171	227323	–41970	50808	402	314	379	325
7000	432540	275012	36083	99376	409	321	391	332

a. [*h*] = J/kmole; [*s*] = J/(K · kmole). Values calculated with property functions in EES (Klein et al., 1991).

SOLUTION: (a) Methane and oxygen combine to form carbon dioxide and water according to

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

With only these substances present in their stoichiometric ratios, the rate of production of entropy turns out to be

$$\Pi_S = \frac{\left|\Pi_{n,fuel}\right|}{T}\left\{\left[\left(\bar{h}_{CH_4} + 2\bar{h}_{O_2}\right)_{T_0} - \left(\bar{h}_{CO_2} + 2\bar{h}_{H_2O}\right)_T\right] - T\left[\left(\bar{s}_{CH_4} + 2\bar{s}_{O_2}\right)_{T_0} - \left(\bar{s}_{CO_2} + 2\bar{s}_{H_2O}\right)_T\right]\right\}$$

while the convective entropy currents at the inlet and the outlet are equal to

$$\left|I_{s,conv,in}\right| = \left|\Pi_{n,fuel}\right|\left(\bar{s}_{CH_4} + 2\bar{s}_{O_2}\right)_{T_0}$$
$$\left|I_{s,conv,out}\right| = \left|\Pi_{n,fuel}\right|\left(\bar{s}_{CO_2} + 2\bar{s}_{H_2O}\right)_T$$

These last two relations provide for a second expression of the rate of production of entropy. Numerical data about the entropies and the enthalpies of the species for different temperatures are given in Table 8.2. Table 8.3 lists the convective entropy currents and the rate of entropy production calculated according to the two forms given above. Since the rates have to be equal at the condition of the adiabatic flame temperature, interpolation in the last two columns gives the desired result (5240 K).

Note that the flame temperature calculated in the manner just presented coincides with the minimum of the entropy production (S_{prod1}) calculated for different temperatures. This is an example of a phenomenon we will discuss in detail in Chapter 9.

(b) In air, there are 3.76 mole of N_2 for every mole of O_2. Therefore, if we write the reaction equation with the theoretical amount of air, it takes the form

$$\mathrm{CH_4} + 2\left(\mathrm{O_2} + 3.76\mathrm{N_2}\right) = \mathrm{CO_2} + 2\mathrm{H_2O} + 2\cdot 3.76\mathrm{N_2}$$

(c) Repetition of the procedure demonstrated in (a) with nitrogen included gives an adiabatic flame temperature of 2330 K. Obviously, having inert nitrogen present changes the result considerably. Even though nitrogen does not take part in the reaction, it has to be heated to the flame temperature, which reduces the effect.

Table 8.3: Entropy transferred and entropy produced[a]

T / K	S_{e_in}	S_{e_out}	S_{prod1}	S_{prod2}
298	596	591	2687	–5
1000	596	734	855	138
2000	596	838	525	242
3000	596	906	443	310
4000	596	957	416	361
5000	596	997	409	401
6000	596	1029	411	433
7000	596	1056	416	460

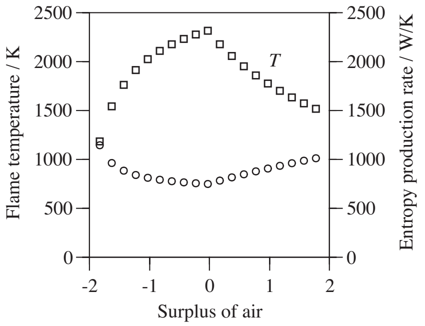
a.$[I_S]$ = J/(K·kmole); $[\Pi_S]$ = J/(K·kmole).

(d) If there is a positive surplus of air (more than the theoretical amount), the reaction equation can be written in the following form:

$$\mathrm{CH_4} + (2+X)\left(\mathrm{O_2} + 3.76\mathrm{N_2}\right) = \mathrm{CO_2} + 2\mathrm{H_2O} + (2+X)3.76\mathrm{N_2} + X\mathrm{O_2}$$

The equation does not apply for negative X. (It has to be changed appropriately to take into consideration that not all methane is burned.) Repeating the calculation for various values of X gives the graph shown below (Fig. Ex.11).The curves for the rate of entropy production (calculated per unit amount of methane burned) and for the adiabatic flame temperature demonstrate that the lowest irreversibility leads to the largest value of the flame temperature.

Figure Ex.11



(e) Look again at the equation for the rate of production of entropy for case (a). The second expression in brackets is, itself, equal to the entropy produced per mole (according to the balance of entropy, Equ.(8.99)). Therefore, the first term in brackets must be zero, proving the statement about the enthalpies of the two fluid streams. We could have started our analysis with this result; however, we wanted to base the derivation upon a consideration of entropy.

EXERCISES AND PROBLEMS

1. A wind power generator having a cross section of $75\,\mathrm{m}^2$ is exposed to winds at a speed of 50 km/h. Behind the rotor, the flow surface increases by a factor of 1.6. The air can be treated as incompressible and with a density of $1.2\,\mathrm{kg/m}^3$. Assume its temperature to remain constant. (a) What is the purely convective energy flow of the wind through the cross section of the rotor? (b) At what rate is the energy transferred to the rotor? (c) The rotor turns at a frequency of 0.5 Hertz. What is the current of angular momentum through the shaft of the wheel to the generator?

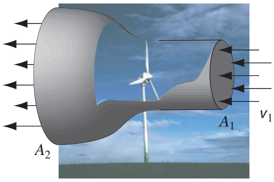


Figure P.1

2. Air having a temperature of 300 K and a pressure of 1.2 bar is flowing through a thermally insulated porous plug with a mass flux of 0.20 kg/s. The duct has diameters of 10 cm and 15 cm at the at the inlet and the outlet, respectively. (a) Calculate the outlet temperature and pressure. (b) What is the entropy production rate?

3. Hydrogen is burned with oxygen in a rocket engine. Knowing that the exit speed of the gas is around 3000 m/s, estimate the temperature of the stream.

4. A pressure vessel of steel having a mass of 8 kg and a volume of 6.0 liters contains 4 liters of water and 0.50 kg of nitrogen gas at a temperature of 20°C. The container stands on three legs. On the bottom of the container is a hole with an automatic valve. (a) What is the pressure of the gas? (b) At what speed does the water flow out of the hole immediately after it is opened? (c) What diameter must the hole have so that the initial acceleration of the vessel is $30\ \mathrm{m/s}^2$?

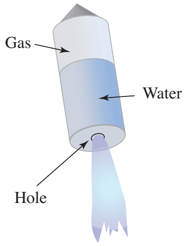


Figure P.4

5. There is hot water in an open tin can. The water flows out through a horizontal pipe. (a) Does the thermal process (entropy flow and temperature change) have an influence upon the hydraulic process, or can the two processes be calculated independent of each other? (b) Consider the water in the can as a system. Formulate the instantaneous balance of mass. (c) Again take the water in the can as the system. With the help of the balance of entropy, prove that the rate of change of temperature is given by

$$m\kappa\dot{T} = -G_S\left(T - T_a\right) + l_v I_{m,v}$$

m is the mass of the water in the system, T is the temperature. κ and G_S denote the specific entropy capacitance and the entropy conductance, respectively. l_v and $I_{m,v}$ are the specific entropy of vaporization and the current of mass of the evaporating water, respectively. T_a stands for the ambient temperature.

6. Consider a solar collector consisting of a black absorbing metal sheet with a surface area of $0.80\ \mathrm{m}^2$ and a rectangular air duct underneath. The flux of mass of air through the duct is 0.10 kg/s. Inlet and outlet temperatures have been measured and are 27°C and 30°C, respectively. Ambient temperature is equal to 17°C. (a) What are the entropy and energy currents with respect to the air? (b) Assume the convective heat transfer coefficient from the absorber to the air in the duct to be $20\ \mathrm{W/(K \cdot m^2)}$. What must the average temperature of the absorber be? (c) Assume the convective heat transfer coefficient from the absorber to the ambient air to be $10\ \mathrm{W/(K \cdot m^2)}$. The metal sheet radiates like a black body. What is the ratio of the heat losses due to radiation and convection to the environment?

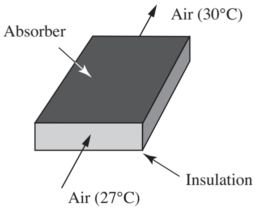


Figure P.6

7. Imagine water having temperature T_f flowing into a tank containing water at a temperature T (the present mass of water is m, and the mass flux is I_m). Heat loss to the environment is determined by an entropy conductance G_S. (a) Formulate the entropy production rate as a result of mixing water at different temperatures. (b) Derive the differential equation for the temperature of water in the tank and solve it.

8. A current of oxygen gas of 20 kg/s is continuously mixed with a current of hydrogen gas of 1.0 kg/s. Use a value of 7/2R for the molar temperature coefficient of enthalpy of both gases. (a) Temperatures and pressures of both streams are 300 K and 1.0 bar, and the pressure of the exit stream is 1.0 bar. Calculate the exit temperature and the rate of entropy production. (b) Repeat the calculation if the temperature of the incoming hydrogen gas is 400

K. (c) Repeat the calculation with the pressure of the incoming hydrogen gas being 2.0 bar (at a temperature of 300 K).

9. Model the heating of the air in a room as follows. As entropy is added to the air, it expands and diffuses through the walls in such a way that it leaves the pressure in the room at a constant value. Now take a constant value for the heating power. Show that, in this case, the temperature of the air rises according to

$$T(t) = T_0 \exp\left(\frac{\mathcal{P}_{heating} t}{7/2PV}\right)$$

if a value of 7/2R is taken for the molar temperature coefficient of enthalpy of air. Note that it is assumed that the air remaining in the room does not lose any heat to the surroundings.

10. Consider the following strongly simplified model of the accretion of a planet. Matter with a temperature T_o falls from far away onto the surface of a growing planet. (The planet is surrounded by a gas of temperature T_o.) Assume the surface of the planet to radiate like a gray body. (a) If the effect of the rate of change of the temperature can be neglected, show that the surface temperature at an instantaneous value of the radius can be calculated using

$$|I_m| c_P (T - T_o) + e 4\pi r^2 \sigma \left(T^4 - T_o^4\right) = |I_m| G \frac{m(r)}{r}$$

where I_m is the flux of mass falling upon the planet, c_P is its specific temperature coefficient of enthalpy, and e is the emissivity of the surface. (*Hint:* Treat the surface as an open control volume and consider the law of balance of energy for this system; first derive the instationary model.) (b) Show that this is equivalent to

$$\rho c_P (T - T_o)\frac{dr}{dt} + e\sigma\left(T^4 - T_o^4\right) = \rho G \frac{m(r)}{r}\frac{dr}{dt}$$

(c) Model accretion by setting the rate of change of the planet's radius equal to[8]

$$\frac{dr}{dt} = k_1 t^2 \sin(k_2 t)$$

At $t = 0$ and at $t = t_a$ (total accretion time) this function is supposed to vanish, and the radius of the planet grows from 0 to R during this period. Show that this leads to the following expressions for the constants k_1 and k_2:

$$k_1 = \frac{R}{t_a^3\left(1/\pi - 4/\pi^3\right)}$$

$$k_2 = \frac{\pi}{t_a}$$

(d) Calculate $T(r)$ for the following values of the parameters. $T_o = 100$ K, $\rho = 5500$ kg/m^3, $c_P = 800$ J/(K · kg), $R = 6.4 \cdot 10^6$ m, $t_a = 5 \cdot 10^5$ years, $e = 1$. (You should get the largest temperature, roughly 1200 K, at a radius of 5000 km.)

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[8] Anderson (1989), p. 3.

CHAPTER 9

MINIMIZATION OF ENTROPY PRODUCTION

In Chapter 4 we learned that loss of power of thermal engines is related to entropy production (Section 4.4.3). This observation suggests that we should avoid—or at least minimize—entropy production if we want to optimize thermal engines. In this chapter I would like to show by example that the idea of minimizing entropy production rates is a powerful principle of thermal design[1] and appears to be useful as well, when analyzing natural systems.Applying this principle is a fitting conclusion to the introductory chapters of this book.

The idea will be described in the following and then applied to a number of processes which are varied enough to demonstrate the wide applicability of entropy generation minimization. The examples are taken from the field of engines (including solar power systems), fluid and heat flow, heat storage, and the Earth's atmosphere.

9.1 MINIMIZATION OF ENTROPY PRODUCTION RATES

When entropy is produced, a loss of available power is inevitable. We can conclude this from the results derived in Section 4.4.3. We were able to quantify the loss in terms of the rate of generation of entropy and the temperature of the body which acts as the final reservoir for entropy; usually this is the environment. For engineers this indicates that a strategy trying to optimize power output or power requirement must try to minimize the production of entropy. While this rule appears to be quite intuitive after all that has been said about the role of entropy in thermal engines, it might be less than obvious in the case of direct heating (without the use of heat pumps). After all, in heating we require the most amount of entropy; so why should we not produce as much as possible of the quantity responsible for making bodies warm? In this section I will demonstrate that the minimization of entropy generation is a goal we generally should try to embrace.

Electric power from fuels. Before we consider the case of direct heating, let us take a brief look at processes that are commonly used to drive electric generators. There are

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[1] The concept of entropy generation minimization has been applied to many engineering systems in recent decades. It has been formulated as a general principle of thermal design (A. Bejan, 1988, 1996; Sieniutycz and de Vos, 2000). The approach has also been applied to models of environmental economics (M. Ruth, 1993).

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_10,

two examples that will make clear the usefulness of strategies for minimizing entropy production: typical thermal power plants and fuel cells.

There is a source of dissipation which, in the case of a standard heat engine that uses chemical fuels, is all but unavoidable. The fuels must be burned to be useful and entropy is produced. This initial irreversibility is the reason for the upper limit on the thermal efficiency of an ideal heat engine—the so-called Carnot efficiency given in Equ.(4.27)—which can be increased only if the higher operating temperature of the engine is raised. This rule is related to the fact that less entropy is produced per unit of energy dissipated if the temperature is raised (Equ.(4.23)).

If we want to avoid the initial irreversibility inherent in thermal engines, we have to consider completely different systems such as fuel cells for harnessing the chemical power of fuels. At least in theory, this should be even better than burning fuels at high temperatures. If ideal fuel cells existed, all the energy released could be made available for the electric process. The reason is simple: the chemical reactions are allowed to run in a manner that does not lead to entropy production (Section 6.5.3). However, since other processes in fuel cells are dissipative, there is room for designing them according to the principle of minimal entropy production.

Using entropy wisely. The major rule to be followed, then, has to do with the use of entropy once it has been generated. If the goal is, for example, heating of water for domestic consumption, direct heating by fire appears to be utter waste. Instead of harnessing the available power of heat we let it conduct to the desired low temperature, which means pure dissipation. If the entropy is used in engines we should likewise avoid any drop in temperature which is not used for the envisioned purpose. Carnot, without knowing much about rates of production of heat in a modern sense, expressed this point succinctly:[2]

> Since every re-establishment of equilibrium in the caloric may be the cause of the production of motive power, every re-establishment of equilibrium which shall be accomplished without production of this power should be considered as an actual loss.

By *re-establishment of equilibrium*, he meant the fall of caloric (entropy) back to a previous thermal level (temperature). We now know how to measure the actual loss, namely as dissipation resulting from entropy production.

It appears that the rule to be given to those who build thermal engines is to avoid any production of entropy. However, in real life, as a consequence of this requirement nothing moves. *Real* processes which run at finite speed are dissipative.[3] Therefore the rule we are looking for must be expressed in the following form:

> *To optimize processes involving heat engines, we must minimize the rate of production of entropy under realistic constraints.*

Direct heating. While the rule of minimal entropy production appears to be fairly straightforward for power processes, it might come as a surprise that it also holds for heating processes. To understand this, we must first define the goal of heating. An op-

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[2] S. Carnot (1824), p. 22.

[3] We considered *ideal* processes which run at finite speed in Chapter 5; they do not produce entropy.

timal heating process delivers the largest amount of entropy for a given heating power to a body at a desired temperature T, where the process takes place in an environment at temperature T_a (see Fig. 9.1). The rule then takes the form:

> *For a fixed heating power, the body to be heated receives the largest amount of entropy if the amount of entropy produced is minimal for the processes involving heating and losses from the furnace.*

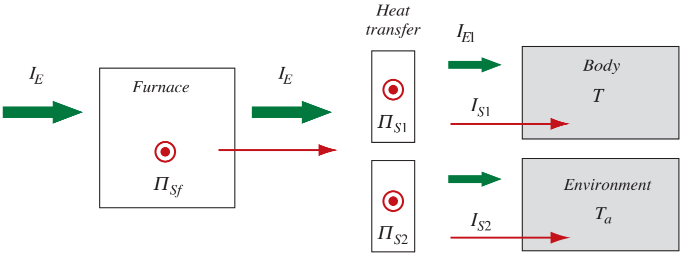


Figure 9.1: A furnace heats a body at a desired temperature T and the environment at T_a (losses). Entropy is produced in the furnace and as a result of heat transfer. The furnace may be of any type, including solar.

The proof goes as follows. The body to be heated at constant temperature T receives an entropy current I_{S1}, while a current I_{S2} is associated with the losses from the furnace. The production of entropy takes place in the furnace (which receives energy at a fixed rate I_E) and as a consequence of heat transfer from the furnace to the body to be heated and to the environment. Altogether, the rate of production of entropy must be equal to the sum of the entropy currents flowing into the body and the environment:

$$\Pi_S = |I_{S1}| + |I_{S2}| \tag{9.1}$$

We can express the second entropy current in terms of the fixed energy current received by the heating system as well as the temperatures involved:

$$\begin{aligned}\Pi_S &= |I_{S1}| + \frac{|I_E| - |I_{E1}|}{T_a} = |I_{S1}| + \frac{|I_E| - T|I_{S1}|}{T_a}\\ &= \frac{|I_E|}{T_a} - \left(\frac{T}{T_a} - 1\right)|I_{S1}|\end{aligned} \tag{9.2}$$

This result demonstrates that the rate of production of entropy decreases as the amount of entropy delivered for heating is increased.

There is a direct relationship between the cases of power engineering and heating. The result demonstrated in Equ.(9.2) can be cast in terms of the available power of heat. If we heat a body at a temperature surpassing that of the environment, we may subsequently use its entropy to drive a heat engine. In other words, we still have some available power which is proportional to both the temperature difference between body and environment and the amount of entropy which can be drawn from the body. Therefore, maximizing the heating of the body in question is equivalent to maximizing the available power of the heating process. Put in these terms, we can appreciate the generality of the rules stated above. Accounting for entropy in all its aspects is not just a convenient theoretical tool, it is the central task of those involved in the use of heat for any purpose.

Consider once again the importance of being able to compute the rate of production of entropy from a constitutive theory. The rule discussed here is nice but completely useless if we do not manage to calculate such quantities as the rate of generation of entropy and currents of entropy for concrete cases. The generic laws which we have been using, i.e. the laws of balance of entropy and energy, alone, do not provide this information.

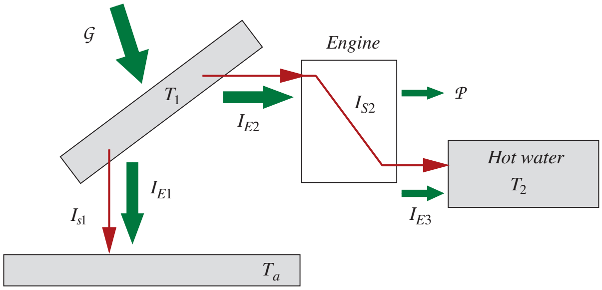
QUESTIONS

1. Why should minimizing the irreversibilities of a system result in a maximum of useful power? What is the role of an environment at a given fixed temperature in this argument?
2. Consider irreversible engines. Does the condition of maximum power always coincide with the condition of minimal entropy production rate?
3. Why should one use fuel cells rather than combustion engines connected to generators (i.e., thermal power plants)?
4. From a thermodynamics standpoint, is it better to use heat pumps than burning fuels for heating a home?
5. Why does minimizing entropy production make sense in a heating process, considering that we want entropy for making a body warm?

EXAMPLE 9.1. Optimizing a solar thermal engine with hot water production.

We can produce heat in a collector by absorbing solar radiation. Assume that the radiation is completely absorbed; also assume that solar radiation does not bring any entropy with it. (This is very nearly true; see Chapter 7.) The hot collector (simply a hot body) emits entropy to an ideal Carnot heat engine and loses heat to the environment at temperature T_a. The loss is modeled in terms of a law such as in Equ.(4.48) with an overall heat loss coefficient h. The engine rejects the entropy received from the collector to a large body of water at a temperature T_2, which is larger than T_a thus providing both power and hot water at T_2.

Figure Ex.1



Take values of 290 K and 330 K for T_a and T_2, respectively. The solar radiation is measured in terms of the energy flux per unit area and is taken to be equal to $\mathcal{G} = 800\ \text{W/m}^2$. The overall heat loss coefficient is $h = 4.0\ \text{W/(K}\cdot\text{m}^2)$. (a) For which value of the temperature of the collector (T_1) will the rate of production of entropy be minimal? Why would you expect a minimum of entropy production at all? (b) How large should the temperature of the collector be for the power of the engine to reach its maximum? (c) Why don't the minimum of entropy production and the maximum of power coincide? Is there a quantity related to power that has a maximum coinciding with the minimum of entropy production? Would you run the system at maximum power or at minimum entropy production?

SOLUTION: (a) The radiation is absorbed by the collector, leading to production of entropy at the temperature of the collector T_1. The rate of absorption of energy from solar radiation ($A\,\mathcal{G}$) is equal to the rate of dissipation. (The collector does not do anything else but produce entropy.) The rate of production of entropy from this source must therefore be equal to $A\mathcal{G}/T_1$. On the other hand, entropy flows from the collector to the environment at T_a, leading to more entropy being produced (see Section 4.6). Hence, the rate of production of entropy in the entire system is made up of these two parts (all other processes proceed reversibly):

$$\Pi_S = \frac{A\,\mathcal{G}}{T_1} + A\,h\left(T_1 - T_a\right)\left[\frac{1}{T_a} - \frac{1}{T_1}\right]$$

The minimum of this function is found by differentiating it with respect to the temperature of the collector:

$$\frac{d\Pi_S}{dT_1} = -\frac{A\,\mathcal{G}}{T_1^2} + A\,h\left[\frac{1}{T_a} - \frac{1}{T_1}\right] + A\,h\left(T_1 - T_a\right)\frac{1}{T_1^2}$$

$$\frac{d\Pi_S}{dT_1} = 0$$

$$\Rightarrow \qquad T_{1,min\ S} = \sqrt{\frac{T_a}{h}\,\mathcal{G} + T_a^2}$$

For the given numerical values, the minimum of production of entropy is obtained for a temperature of 377 K. We expect the rate of production of entropy to have a minimum because it should be large for both small and large values of the temperature of the collector but for opposing reasons. At high T_1, the rate of production inside the collector will be small while the losses, and therefore the entropy production due to the flow of heat, must be large. At small values of T_1 we have exactly the opposite conditions. Since the effects are nonlinear we can expect a function with a minimum.

(b) The balance of energy for the collector operating at steady-state is given by

$$I_{E2} = A\,\mathcal{G} - A\,h\left(T_1 - T_a\right)$$

With the help of the relationship between the current of entropy and the current of energy transferred to the heat engine,

$$I_{E2} = T_1 I_{S2}$$

we can now express the power of the engine:

$$\begin{aligned}\mathcal{P} &= \left(T_1 - T_2\right) I_{S2} \\ &= \frac{T_1 - T_2}{T_1} I_{E2} \\ &= \frac{T_1 - T_2}{T_1}\left[A\,\mathcal{G} - A\,h\left(T_1 - T_a\right)\right]\end{aligned}$$

Its derivative with respect to the temperature of the collector will yield the condition for maximum power:

$$\frac{d\mathcal{P}}{dT_1} = \frac{T_2}{T_1^2}\left[A\,\mathcal{G} - A\,h\left(T_1 - T_a\right)\right] - \frac{T_1 - T_2}{T_1} A\,h$$

$$\frac{d\mathcal{P}}{dT_1} = 0 \quad \Rightarrow \quad T_{1,\,max\;P} = \sqrt{\frac{T_2}{h}\mathcal{G} + T_2 T_a}$$

The numerical value is 402 K. The expressions for the minimum of entropy production and the maximum power of the engine will only be the same if the "hot water" produced has the same temperature as the environment.

(c) The rule that minimal production of entropy should deliver maximum output from engines holds only for a single reservoir into which entropy is rejected. In this example, the entropy produced by the absorption of sunlight ends up in two environments which have different temperatures. The loss cannot be calculated by choosing one of the temperatures and multiplying it with the rate of production of entropy. The entropy current rejected to the hot water still represents some available power. We can interpret the power of the engine as being 100% "pure" availability. Therefore, if we add it to the available power of the current of entropy at T_2, we have a quantity whose maximum can be shown to coincide with the minimum of entropy production.

9.2 A MODEL OF AN ENDOREVERSIBLE ENGINE

Only a few decades ago, the following model of heat engines was proposed as a more realistic alternative to the ubiquitous ideal Carnot engine.[4] The major drawback of the Carnot engine has not so much to do with the processes undergone by the working fluid but with the rate of transfer of entropy from the furnace to the engine, and from the engine to the cooler. For these rates to be finite there must be finite temperature differences if we think of transferring entropy conductively. No realistic heat exchanger will work without such a drop of temperature. We may then run an ideal Carnot engine between temperatures which are somewhat lower than that of the furnace and somewhat higher than that of the cooler, respectively (Fig. 9.2). Entropy conducted from the furnace and to the cooler causes dissipation in the combined system of heat exchangers plus Carnot engine. We must face the reality that we either have a completely ideal engine at zero power, or a nonideal device at finite power. What we can realistically strive for is an engine that operates with a *minimum rate of production of entropy*. There should be a minimum of entropy generation in the model engine proposed in Fig. 9.2. If we do not allow for any temperature gaps between the heat exchangers and the Carnot engine, the energy supplied from heating simply leaks directly to the environment (cooler) and we have total dissipation. The same situation arises if the upper and the lower operating temperatures of the ideal Carnot engine are made equal. Somewhere between these two extremes must lie the optimum condition for the smallest possible rate of production of entropy and the largest mechanical power. Let us look for it.

The model engine works as follows (Fig. 9.2). It is heated from the furnace at a constant rate. In general, the engine can absorb part of the current, the fraction being de-

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[4] The type of heat engine called *endoreversible* was first proposed and analyzed by Curzon and Ahlborn (1975). They calculated the power of the engine and determined the condition for its maximum. The efficiency at maximum power, Equ.(9.12), has since been called the Curzon-Ahlborn efficiency. A simpler derivation was given by DeVos (1985). The problem was later investigated from the point of view of the minimization of the production of entropy (Salamon et al., 1980; Andresen et al., 1984).

termined by the rate at which entropy can flow through the heat exchanger (represented by the thermal resistor *R*1) to the ideal Carnot engine. The rest of the entropy flux will leak directly to the environment via the thermal resistor *R*3. The core of the engine, i.e. the ideal Carnot heat engine, will reject the entropy at the lower operating temperature, thereby releasing energy in the mechanical process. The heat exchanger serving the cooler (represented by the thermal resistor *R*2) must be designed to handle this current of entropy. Naturally, once we have found the condition for maximum mechanical power and the flux of entropy associated with it, we will adjust the current of entropy from the furnace to this value to avoid unnecessary leakage through *R*3. Because of the reversible Carnot engine at the core of the system the entire model has been called an *endoreversible engine*.

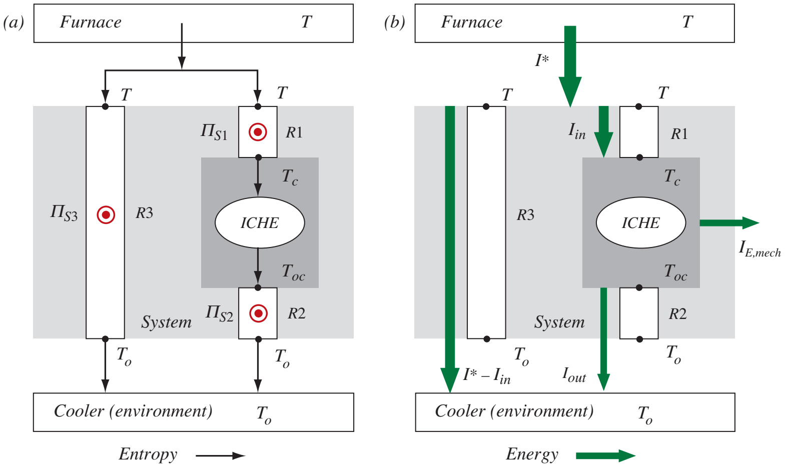

Figure 9.2: (a) The flow of entropy (solid arrows) in a system which contains an ideal Carnot heat engine (*ICHE*) and conductive resistances. The system is heated at a constant rate from the furnace. Due to the resistances of the heat exchangers to the *ICHE*, the flow of entropy in this branch is limited. Entropy is produced in the resistors. (b) Energy flow diagram. The energy currents associated with the currents of entropy are shown as heavy arrows. It is found that minimizing the rate of production of entropy in the composite system will maximize the mechanical power.

We need to be able to calculate the effect of the heat exchangers included with the model engine. It is important for us to know that the form of the simplest constitutive law for heat transfer through an exchanger, Equ.(4.48), is quite applicable to our case. Since we will find that the maximum efficiency of our model engine does not to depend upon the coefficient multiplying the difference of temperatures, we do not have to worry about the actual transport processes.

We can now turn to the job of first calculating and then minimizing the rate of production of entropy in the system of Fig. 9.2. The only dissipative elements in the engine are the three thermal conductors, i.e. the heat exchangers and the machine itself, which leaks entropy. The rate of production of entropy is equal to the sum of the rates due to the three resistors:

$$\Pi_S = \Pi_S(R1) + \Pi_S(R2) + \Pi_S(R3) \tag{9.3}$$

As before, we calculate the production rates for steady-state conditions in terms of the fluxes of entropy entering and leaving the bodies. In the following equations, all fluxes represent absolute values, and, for convenience, the index *E* has been dropped from the thermal energy currents. The overall rate of generation of entropy can be expressed as follows:

$$\Pi_S = I_{in}\left(\frac{1}{T_c} - \frac{1}{T}\right) + I_{out}\left(\frac{1}{T_o} - \frac{1}{T_{oc}}\right) + (I^* - I_{in})\left(\frac{1}{T_o} - \frac{1}{T}\right) \tag{9.4}$$

Four variables appear in this equation, namely the energy currents entering and leaving the Carnot engine, and the upper and the lower operating temperatures of the ideal engine. The total thermal energy current I^* and the temperatures of the furnace and the cooler are assumed to be fixed. We would like to eliminate three of the variables and leave only the thermal energy current entering the Carnot engine in the equation. The three elements of interest in our model system, namely the Carnot engine and the two heat exchangers, furnish the necessary conditions. Since the engine operates without dissipation, the current of entropy entering is equal to the current being emitted. This leads to

$$\frac{1}{T_c} I_{in} = \frac{1}{T_{oc}} I_{out} \tag{9.5}$$

The heat exchangers operate according to the simple constitutive law, Equ.(4.48), which means that

$$I_{in} = a\left(T - T_c\right) \tag{9.6}$$

and

$$I_{out} = b\left(T_{oc} - T_o\right) \tag{9.7}$$

The coefficients a and b are assumed to be constants. After eliminating these three variables, the production rate of entropy is expressed in the single variable I_{in}:

$$\Pi_S = I^*\left(\frac{1}{T_o} - \frac{1}{T}\right) - \frac{1}{T_o} I_{in}\left[1 - \frac{bT_o}{bT - \left(1 + b/a\right)I_{in}}\right] \tag{9.8}$$

You will notice that the fixed heating power I^* does not contribute to the condition for the minimal generation rate we are going to calculate. Now we are ready to compute the derivative of this expression with respect to the energy flux entering the Carnot engine:

$$\begin{aligned} \frac{d\Pi_S}{dI_{in}} = &-\frac{1}{T_o}\left[1 - \frac{bT_o}{bT - \left(1 + b/a\right)I_{in}}\right] \\ &+ \frac{1}{T_o} I_{in} \frac{bT_o}{\left[bT - \left(1 + b/a\right)I_{in}\right]^2}\left(1 + \frac{b}{a}\right) \end{aligned} \tag{9.9}$$

Setting the derivative equal to zero will deliver the condition for the energy flux at the minimum rate of entropy production. After some lengthy algebra we get a quadratic equation for I_{in} whose solution is

$$I_{in}\left(max\right) = \frac{ab}{a + b}\left[T - \sqrt{T\,T_o}\right] \tag{9.10}$$

This should represent the thermal power at the upper operating temperature of the Carnot engine for *maximum mechanical power*. It depends upon the temperatures of the furnace and the cooler, and on the physical properties of the heat exchangers which are expressed by the factors *a* and *b*. The mechanical power itself is calculated according to the rules for ideal Carnot engines (Section 4.4.3) leading to

$$I_{mech}(max) = I_{in}(max)\left[1 - \frac{abT_o}{abT - (a+b)I_{in}(max)}\right] \tag{9.11}$$

More significantly, the efficiency of the model engine at maximum power is independent of the dimensions of the heat exchangers. Just as in the case of the ideal Carnot engine, it depends only upon the temperatures of furnace and cooler:

$$\eta_{1,max} = 1 - \sqrt{\frac{T_o}{T}} \tag{9.12}$$

This is the result reported by Curzon and Ahlborn.[5] The original derivation was done in terms of the power of the engine whose maximum had to be determined. Today we know that engines designed for maximum power obviously follow a basic principle, namely minimizing production of entropy.

It is instructive to compare the actual efficiencies of a number of thermal power plants (Fig. 9.3). It appears that they rather closely approach the efficiency of the model engine in Fig. 9.2. The determining factor in such devices seems to be the transfer of entropy to and from the actual engine, while the behavior of the fluid driving the engine can be regarded as almost ideal.

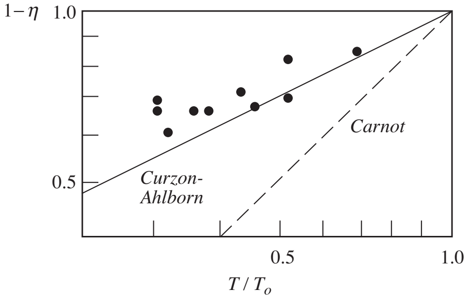

Figure 9.3: Observed efficiencies of thermal power plants are plotted as a function of the ratio of the temperatures of the furnace and the cooler. The broken line on the right represents the efficiency of ideal Carnot engines. The theoretical efficiency according to Equ.(9.12) is drawn as the straight line to the left. The figure has been drawn after Bejan (A. Bejan, 1988, p. 409).

This is an example of what has become the focus of interest in so-called *finite-time thermodynamics* in recent years. Finite-time thermodynamics[6] develops simple aggregate models of dissipative processes. As such, it may be called a part of the modern approaches which deal with processes rather than just states. Like continuum thermodynamics, it demonstrates that a dynamical theory of heat can do more than just find equilibrium values in thermal systems. Armed with an intuitive understanding of entropy, we can do so much more than in classical thermodynamics.

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[5] Curzon and Ahlborn (1975).

[6] For example, see J.M. Gordon (1990), and references therein.

QUESTIONS

6. What is the meaning of *endoreversible*? What is an endoreversible Carnot engine?
7. Use the model shown in Fig. 9.2. Why doesn't an engine run if it makes use of the entire temperature difference between T and T_o?
8. A power plant has upper and lower temperatures of 600 K and 300 K, respectively, and an efficiency of 32%. How closely does it perform to the formula of Curzon and Ahlborn?

EXAMPLE 9.2. Designing a thermal power plant at maximum power.

The Dungeness nuclear reactor built in Great Britain in 1965 performs very closely to the rule given for thermal plants at maximum power, Equ.(9.12). The temperatures of its furnace and cooler are 663 K and 298 K, respectively. Assume a plant of this type to be designed for 500 MW mechanical power. (a) How large must the heating power from the reactor be for the plant to operate at maximum power? (b) Assume the heat transfer coefficients of both heat exchangers to be equal (i.e. their physical characteristics are taken to be the same). Furthermore, take the exchangers to be equally large. How large is the effective surface area of each of the heat exchangers if the transfer coefficient has a magnitude of 1000 W/(K·m^2)? (c) Determine the upper and the lower operating temperatures of the Carnot engine for the heat exchangers designed according to (b). (d) With fixed and equal heat transfer coefficients for both heat exchangers, is there a better way of distributing the available surface area than to make both exchangers equally large?

SOLUTION: (a) The efficiency at maximum power of the endoreversible engine is given by Equ.(9.12). Here it turns out to be

$$\eta_{1,max} = 1 - \sqrt{\frac{T_o}{T}} = 1 - \sqrt{\frac{298}{663}} = 0.33$$

This figure determines the magnitude of the heating power necessary for optimal operation. If we can avoid direct leakage of entropy, the requirement for the energy flux from the reactor is simply equal to

$$I_{in}(max) = \frac{I_{mech}(max)}{\eta_{1,max}} = \frac{500\text{MW}}{0.33} = 1.52 \cdot 10^9\,\text{W}$$

(b) According to Equ.(9.10), the dimensions of the heat exchangers and the temperatures of furnace and cooler, determine the heating power. Alternatively, $ab/(a+b)$ in Equ.(9.10) is determined by the data given so far. With $a = b$ we obtain

$$a = 2\frac{I_{in}(max)}{T - \sqrt{T\,T_o}} = 2\frac{1.52 \cdot 10^9}{663 - \sqrt{663 \cdot 298}}\frac{\text{W}}{\text{K}} = 1.39 \cdot 10^7\,\frac{\text{W}}{\text{K}}$$

If the heat transfer coefficient has the magnitude stated above, the surface area of each of the heat exchangers should be $1.39 \cdot 10^4$ m^2.

(c) The operating temperatures of the Carnot engine can be determined from the relations for the rate of transfer of entropy (or energy) according to Equations (9.6) and (9.7). The formal solutions are:

$$T_c = T - \frac{1}{a} I_{in}(max)$$

and

$$T_{oc} = \frac{bT - \dfrac{b}{a} I_{in}}{bT - \left(1 + \dfrac{b}{a}\right) I_{in}} T_o$$

which lead to numerical values of 554 K and 371 K, respectively.

(d) It appears to be reasonable to measure the cost of the heat exchangers in terms of their required surface area. We are therefore looking for the minimum total surface area delivering the desired (fixed) output of the engine. In other words, we are looking for the minimum of $x = a + b$ subject to fixed I_{in}. The surface areas are determined by Equ.(9.11):

$$\frac{x}{a(x-a)} = \frac{T - \sqrt{T T_o}}{I_{in}(max)} \equiv c$$

The minimum of x is found for $a = 2/c$ which yields $x = 4/c$ and $b = a$. In other words, if we have to limit the total surface area of the heat exchangers, we should build them to be of equal surface area at the hot and the cool ends of the engine.

9.3 MAXIMUM POWER OF A SOLAR THERMAL ENGINE

A question of practical interest is how much of the energy radiated to us by the Sun could possibly be released for mechanical purposes by a heat engine. On the one hand, we are used to very low efficiencies of commercial photovoltaic cells (little more than 10%); on the other hand we know that solar radiation transports entropy at a very high temperature, which suggests a large value of the Carnot efficiency. At a temperature of 5800 K for the entropy of radiation arriving from the Sun, we obtain $\eta_C = 1 - 300$ K / 5780 K = 0.95 for the thermal efficiency of an ideal Carnot engine (see Chapter 4). Here we have taken the temperature of the environment on Earth to be 300 K. In other words, the available power of solar radiation is very high, which tells us that we should use solar radiation as a high temperature source in thermal engines.

It is clear that it is impossible to achieve this kind of efficiency, even in theory. Radiative transfer is dissipative by nature. To achieve finite rates of transfer, we need differences of temperatures between the Sun and the receiver on Earth. Even if we could build an ideal Carnot engine between these heat transfer elements, it would achieve a thermal efficiency smaller than the 95% calculated above.

The statement of the problem reminds us of the model engine discussed in Section 9.2, which we constructed to run at maximum power. We can do just the same in the case of a solar thermal engine (Fig. 9.4).

Consider the following simplified model (Fig. 9.4). First of all, we need a concentrator for the sunlight to recreate conditions of the radiation field found at the surface of the Sun. In other words we have to use mirrors which concentrate light in such a manner as to make the solid angle (see Chapter 12) from which radiation flows towards the absorber 2π (equivalent to radiation from a hemisphere). Under these conditions, a blackbody absorber could reach the same temperature T_s as that of the surface of the Sun. However, if this were the case, the net rate of transfer of entropy between the absorber and the Sun would drop to zero. To obtain a finite rate, the absorber's temperature must be smaller than the maximum T_s. For the same reason, the engine will not be able to absorb the entire flux of entropy from the Sun which has been concentrated by the mirrors. A part of the current will be radiated into the environment, which has a temperature of about 300 K (T_o). Since the heat engine is assumed to be ideal, it rejects the same amount of entropy to the environment that it absorbs from the concentrators. Let us neglect the irreversibility of the transfer of heat taking place at the cooler; we simply assume the lower operating temperature of the engine to be T_o. Entropy will be produced due to radiative transfer from the concentrators to the absorber, and from the mirrors to the environment (Fig. 9.4).

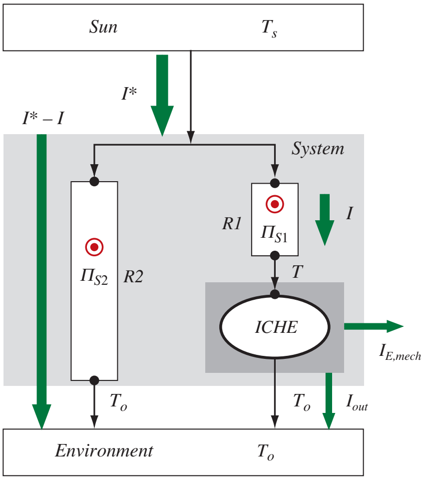

Figure 9.4: An ideal Carnot heat engine (*ICHE*) absorbs entropy from the light concentrated by the mirrors. Because of perfect concentration, the radiation serves as an entropy reservoir at T_s, the surface temperature of the Sun. Since the upper operating temperature is smaller than T_s, part of the entropy will be radiated to the environment. Both elements of heat transfer constitute thermal resistors in which entropy is produced. The engine will achieve maximum power for minimal rate of production of entropy.

The power of the engine will depend upon two factors—the size of its absorber and the upper operating temperature T. We expect the maximum power per unit absorber area to coincide with the minimal rate of entropy production. Therefore we have to express this rate in terms of the temperatures involved. Just as in examples treated before, the rate of entropy production in a heat transfer element is given by the energy flow through the element, and by the upper and the lower temperatures, respectively. If I^* is the energy current from the collectors, a part I will be absorbed by the engine. As a result, the rate of entropy production is

$$\Pi_S = \left(I^* - I\right)\left(\frac{1}{T_o} - \frac{1}{T_s}\right) + I\left(\frac{1}{T} - \frac{1}{T_s}\right) \tag{9.13}$$

The flux of energy absorbed by the engine depends on its surface area and on the temperatures T_s and T:

$$I = \sigma A\left(T_s^4 - T^4\right) \tag{9.14}$$

If we insert this expression into Equ.(9.13), we obtain the rate of production of entropy in terms of the unknown temperature T. We have only to determine the derivative of Π_S with respect to T and set the result equal to zero, which yields

$$\frac{4}{T_o}T^5 - 3T^4 - T_s^4 = 0 \tag{9.15}$$

The solution of this nonlinear equation may be obtained by numerical methods. For values of $T_s = 5762$ K and $T_o = 300$ K, the upper operating temperature of the heat engine turns out to be 2465 K, which corresponds to a thermal efficiency of $\eta_1 = 0.88$. This value is smaller than the one calculated above for a completely reversible engine. However, it is still very large, which again stresses the point that solar radiation should not in every case be wasted for low temperature applications. Some existing solar thermal power plants in the US reach efficiencies around 25%, a number which compares favorably with current photovoltaic elements.[7]

9.4 ANALYSIS OF A SOLAR AIR HEATER

We have studied the occurrence of minimal entropy production rates in heating systems and in thermal engines. It turns out that in these cases, minimal irreversibility is directly or at least closely related to the maximum of the available power of heat. Here is an example that demonstrates that we can find a minimum of irreversibility in the operation of a system even though energy considerations do not provide an optimum.

We want to know if an air-cooled solar collector should be built long and narrow or short and wide. For practical purposes, this question asks whether we should connect a number of panels in series or in parallel to get an optimal effect.[8] To build a model, we shall consider a thin and wide rectangular duct through which air is pumped. The upper side of the duct serves as the absorber of solar radiation. The lower side is perfectly insulated. The collector will be operated so that it delivers air at a prescribed fixed outlet temperature for fixed given inlet temperature. This means we have to adjust the flux of mass of air through the collector when the length to width ratio is changed.

The air will be treated as an ideal gas having constant specific heats. We will consider steady-state conditions in our models unless otherwise stated. The models will be single-node spatially homogenous representations of the systems. This means, for example, that the temperature of the air in the collector has a single value that is assumed to be equal to the outlet temperature.

In the following sub-sections, I will present two derivations of the same model. The first takes the common approach found in engineering thermal design: the model is formulated on the basis of energy considerations and the results are used to calculate the overall entropy production rate for the entire systems. The second approaches the problem directly by expressing entropy currents and entropy production rates for every particular irreversible process and then finding the minimum of the total entropy production rate. As mentioned above, the model provides a very interesting example of Second Law analysis, i.e., an analysis based upon entropy, where considerations of energy or power do not yield an optimal result.

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[7] These SEGS power plants running in California are a commercial success. They use linear parabolic concentrators that reach a concentration factor of about 40. Steam is produced at a temperature approaching 400°C. Currently, plants with a combined power of roughly 350 MW have been installed, and several more plants of the same basic design are being constructed.

[8] This question was first considered by Oppliger (1993). Here I will present a simplified version of his model.

9.4.1 The Balance of Energy

Performing a steady-state balance of energy on the absorber and the air in the duct lets us relate temperatures and energy fluxes. The energy fluxes with respect to the absorber and the air are shown in Fig. 9.5.

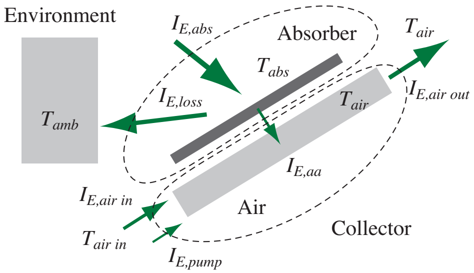

Figure 9.5: An air-cooled solar collector is divided into two separate systems—the absorber and the air. The figure shows the energy fluxes with respect to the systems. I_E denotes an energy flux and T denotes temperatures.

In steady-state, the sum of all energy fluxes with respect to a system must be zero. Here we have two systems—absorber and air. There are three energy fluxes with respect to the absorber: the rate of absorption of energy $I_{E,abs}$, the flux due to heat loss $I_{E,loss}$, and the rate of transfer of energy to the air $I_{E,aa}$. For this system, the balance of energy states that

$$0 = I_{E,abs} - I_{E,loss} - I_{E,aa} \tag{9.16}$$

In the case of the air it takes the form

$$0 = I_{E,aa} + I_{E,air\,in} - I_{E,air\,out} + I_{E,pump} \tag{9.17}$$

Here, $I_{E,air\ in}$ and $I_{E,air\ out}$ represent the convective energy fluxes carried with the air entering and leaving the collector. $I_{E,pump}$ is equal to the power of the pump that makes the air flow through the collector duct.

Constitutive laws for the energy fluxes. We need constitutive expressions for the energy fluxes in order to make use of the laws of balance in Equations (9.16) and (9.17). The rate of absorption of energy is commonly expressed as a fraction $(\tau\alpha)$ of the insolation which is the product of the irradiance $\mathcal{G}$ and the surface area A of the absorber:

$$I_{E,abs} = (\tau\alpha) A \mathcal{G} \tag{9.18}$$

$(\tau\alpha)$ is called the transmission-absorption factor of the absorber (including glass covers). The collector's loss to the environment and the rate of transfer to the fluid in the duct are written in terms of the temperature differences and an energy conductance which is the product of a heat transfer coefficient and the surface area:

$$I_{E,loss} = AU_L (T_{abs} - T_{amb}) \tag{9.19}$$

$$I_{E,aa} = AU_{aa} (T_{abs} - T_{air}) \tag{9.20}$$

where

$$U_{aa} = U_{aa,o} + k\nu \tag{9.21}$$

U_L and U_{aa} are the heat transfer coefficients due to loss and transfer to the fluid, respectively. The latter is a linearly increasing function of fluid speed ν in our model. To obtain the desired outlet temperature for given fixed inlet temperature, the fluid speed has to increase as the collector is made longer. The fact that the efficiency of heat transfer increases with increasing flow speed will play an important role in the interpretation of the results.

In Equ.(9.17), we have the net convective flux due to energy transport with the fluid. For an ideal gas, this is

$$I_{E,air\,in} - I_{E,air\,out} = c_P I_m \left(T_{air\,in} - T_{air} \right) \tag{9.22}$$

(see (8.62)). c_p and I_m are the specific heat at constant pressure and the mass flux of the air, respectively. We still need to calculate the pumping power. It is determined from a model of turbulent flow through the rectangular duct. The output of the model is the pressure drop as a function of fluid speed. We can calculate the pumping power from the pressure drop ΔP and the mass flux I_m:

$$I_{E,\,pump} = \Delta P \frac{I_m}{\rho} \tag{9.23}$$

ρ is the density of the air obtained from the equation of state of the ideal gas. The pumping power increases strongly as the collector is made longer and narrower.

The equations presented so far suffice to compute temperatures and energy fluxes. The total convective energy flux $I_{E,conv} = I_{E,air\ out} - I_{E,air\ in}$ and the net gain $I_{E,conv} - I_{E,pump}$ are of particular interest. From an energy viewpoint, the net gain makes eminent sense: it tells us how much energy is provided by the system. It is clear that we have to pump harder as the collector is made longer and narrower, so we might expect the net energy carried by the air flowing out of the collector to increase with increasing collector length (Fig. 9.6). It might come as a surprise, though, that the net energy gain also increases monotonically as a function of the length of the collector. There is no indication of an optimal value of the length of the collector on the basis of energy quantities.

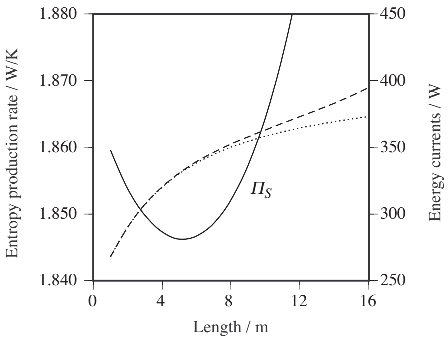

Figure 9.6: Total convective flux (dashed line), energy gain (dotted line), and entropy production rate (solid line) of the system as a function of length of the collector. The results have been calculated for constant irradiance and for a surface area of one square meter. Results have been calculated for turbulent flow of the air and for a particular set of parameters.

9.4.2 The Balance of Entropy

Optimal thermal design is based upon the condition of minimal irreversibility, i.e., minimal entropy production. Sometimes, minimal entropy production and optimal values of energy quantities coincide, but in our example they do not. This makes a Second Law analysis all the more important.

The law of balance of entropy is used to calculate the rate of production of entropy of a system. In the steady-state, all the entropy fluxes I_S and the rate of entropy production Π_S in the system (Fig. 9.7) must add up to zero:

$$0 = I_{S,rad} + I_{S,air\,in} - I_{S,air\,out} - I_{S,loss} + \Pi_S \tag{9.24}$$

Entropy fluxes and entropy production rates are measured in W/K. If constitutive expressions are introduced into this equation, we have

$$\Pi_S = -\frac{4}{3}\frac{(\tau\alpha)A\mathcal{G}}{T_{sun}} + \left[c_P \ln\left(\frac{T_{air}}{T_{air\,in}}\right) - \frac{R}{M_0}\ln\left(\frac{P_{air}}{P_{air\,in}}\right)\right] I_m - \frac{I_{W,loss}}{T_a} \tag{9.25}$$

(see Chapters 7 and 8). R is the universal gas constant and M_0 is the molar mass of the ideal gas. The first term represents the entropy flux carried by the radiation of the Sun, the second is the net convective entropy current carried by the air, and the third equals the entropy current into the environment. The entropy production rate can now be calculated for the steady-state processes undergone by our collector (see Fig. 9.7). This result demonstrates that there is a condition for optimal thermal design: the entropy production rate is found to be minimal at a certain value of the length of the collector (see Fig. 9.6).

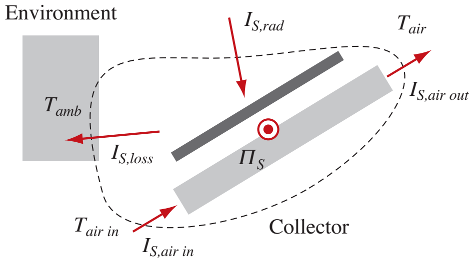

Figure 9.7: The system used to perform the Second Law analysis includes the collector and a part of the environment. This ensures that all relevant contributions to the entropy production are part of the system.

9.4.3 Revisiting the model

We now employ the direct approach for modeling the collector. To do so, we have to consider all the processes taking place and determine entropy transfers and irreversibilities. The processes taking place are (1) absorption of radiation, (2) entropy loss to the environment due to convection and radiation, (3) entropy transfer from the absorber to the fluid, (4) convective entropy transfer and mixing and (5) fluid friction. As a result we have five sources of entropy production (Fig. 9.8).

The laws of balance of entropy for the absorber and the air in the duct take the following forms in steady-state:

$$0 = I_{S,rad} - I_{S.aa} - I_{S,loss} + \Pi_{S1} \tag{9.26}$$

$$0 = I_{S,aa} - I_{S,conv} + \Pi_{S3} + \Pi_{S4} + \Pi_{S5} \tag{9.27}$$

In Equ.(9.27), $I_{S,conv}$ denotes the net convective entropy current. The fluxes appearing in the laws of balance are given by the following constitutive expressions. The entropy carried by solar radiation is

$$I_{S,rad} = \frac{4}{3}\frac{(\tau\alpha)AG}{T_{sun}} \tag{9.28}$$

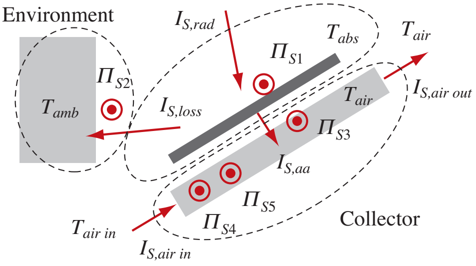

Figure 9.8: Entropy transfers and entropy production in the model of the air-cooled solar collector. There are five processes, all of which are irreversible. Four of these are associated with entropy transfers and mixing, the fifth is due to fluid friction.

The entropy current going from the hot absorber to the cooler air is determined by the associated energy current and the temperature of the absorber:

$$I_{S,aa} = \frac{AU_{aa}}{T_{abs}}\left(T_{abs} - T_{air}\right) \tag{9.29}$$

The expression for the entropy current to the environment follows from the same considerations:

$$I_{S,loss} = \frac{AU_L}{T_{abs}}\left(T_{abs} - T_{amb}\right) \tag{9.30}$$

Finally, we need the expression for the net convective entropy flux which is found from Equations (8.9) and (8.52):

$$I_{S.conv} = \left(-\frac{R}{M_0}\ln\left(\frac{P_{air}}{P_{air\,in}}\right) + c_P \ln\left(\frac{T_{air}}{T_{air\,in}}\right)\right) I_m \tag{9.31}$$

Finally, we determine the five entropy production rates and their sum total. These rates have been calculated before in Chapters 7 and 8:

$$\Pi_{S1} = \left(\frac{1}{T_{abs}} - \frac{4}{3}\frac{1}{T_{sun}}\right) I_{E,abs} \tag{9.32}$$

$$\Pi_{S2} = T_{abs} I_{S,loss}\left(\frac{1}{T_{amb}} - \frac{1}{T_{abs}}\right) \tag{9.33}$$

$$\Pi_{S3} = T_{abs} I_{S,aa}\left(\frac{1}{T_{air}} - \frac{1}{T_{abs}}\right) \tag{9.34}$$

$$\Pi_{S4} = I_m \frac{R}{M_0}\ln\left(\frac{p_{air\,in}}{p_{air}}\right) + c_P I_m\left(\frac{1}{T_{air}}\left(T_{air\,in} - T_{air}\right) - \ln\left(\frac{T_{air\,in}}{T_{air}}\right)\right) \tag{9.35}$$

$$\Pi_{S5} = \frac{I_{E,pump}}{T_{air}} \tag{9.36}$$

The total entropy production rate is the sum of these five terms:

$$\Pi_S = \Pi_{S1} + \Pi_{S2} + \Pi_{S3} + \Pi_{S4} + \Pi_{S5} \tag{9.37}$$

The energy quantities we are interested in can be calculated on the basis of the entropy quantities and the temperatures. The results of the model are the same as those already presented in Fig. 9.6: there is a minimum entropy production rate for a certain ratio of length to width of the collector. While the energy yield gets better and better as we make the collector longer and longer, our consideration of irreversibilities tells us that an optimal design actually exists.

This behavior can be understood quite easily. The low value of the energy current at small lengths is due to high thermal losses; its continued increase with growing length is the result of the increase of the heat transfer coefficient between absorber and fluid. If the collector is made longer, the flux of air must be made larger to maintain a constant temperature at the outlet. Even though the thermal performance continues to improve with increasing length, long collectors (i.e., collectors placed in series) are basically heated by the pump instead of the Sun. Analysis of irreversibility tells us that this strategy is not worth pursuing.

QUESTIONS

9. The net energy current of the collector equals the energy gained from the sun. Why does this gain continue to increase if the collectors length is increased (at constant area)?
10. The total energy gained by the collector (from the Sun and from pumping) increases monotonically as a function of length of the collector (Fig. 9.6); there is no optimum for a certain length. Since the energy for pumping that comes from electricity is valued differently than thermal energy (typically, it is three times as expensive per unit), could one possibly find an economic optimum of the problem?

EXAMPLE 9.3. The balance of entropy for an electric flow heater with heat loss.

A fluid such as water is heated electrically while flowing through a pipe. Assume the temperature of the fluid to increase linearly along the pipe from ambient temperature to a maximum value at the outlet. There is heat loss to the environment. Take the average of the product of the heat loss coefficient and surface area of the pipe to be 20 W/K; the ambient temperature is 293 K, and the value of c_p is 4200 J/(K·kg). The electrical power is 1000 W. (a) Estimate the total rate of production of entropy by writing down the equation of balance for this quantity, using the flux of mass as a parameter. (b) Show that the rate of production of entropy has a minimum for a particular value of the mass flux of the fluid.

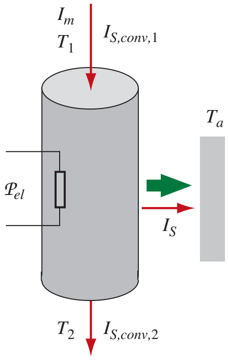

Figure Ex.3.1

SOLUTION: (a) The equation of balance of entropy for the control volume shown in the upper figure (Fig. Ex.3.1) takes the form

$$-\left(I_{S,conv,1} - I_{S,conv,2} - I_S\right) = \Pi_S$$

If we assume the boundary of the control volume touches the surroundings at ambient temperature, the contribution to the production of entropy due to heat loss will be included. The sum of the convective entropy currents is

$$c_p \left|I_m\right| \ln\left(\frac{T_2}{T_1}\right)$$

The current of entropy entering the environment at T_a can be determined by

$$\frac{1}{T_a} UA \left(\frac{1}{2}\left(T_1 + T_2\right) - T_a\right)$$

UA is the product of heat transfer coefficient and surface area. The temperature of the fluid losing heat has been approximated by the arithmetic mean of inlet and outlet temperatures.

We still need to know the outlet temperature of the fluid. It can be calculated using the law of balance of energy:

$$c_p \left|I_m\right| \left(T_1 - T_2\right) + UA\left(\frac{1}{2}\left(T_1 + T_2\right) - T_a\right) = \left|\mathcal{P}_{el}\right|$$

(b) Even though the equations do not look all that complicated, finding the minimum of the rate of production of entropy is best accomplished numerically. The graph in Fig. Ex.3.2 shows this quantity as a function of the flux of mass through the heater.

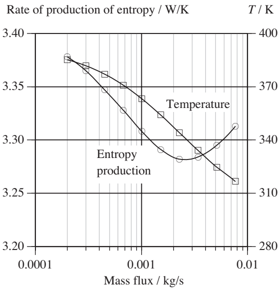

Figure Ex.3.2

9.5 CHARGING AND DISCHARGING A HEAT STORAGE SYSTEM

The problem of minimizing entropy production also occurs in time-dependent problems involving the storage of entropy. Again, rather than delivering some theory, I will treat an interesting example.

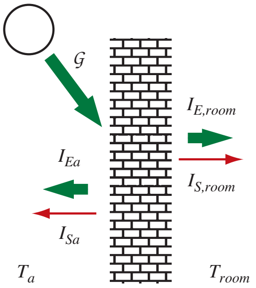

Figure 9.9: Solar radiation absorbed by a wall leads to three sources of irreversibility. One is associated with the absorption of radiation. The other two have to do with heat flow into the environment and into the room.

Consider a building having a heat storage wall. In fact, just consider the wall itself, which obtains heat from the Sun and discharges heat both to the surroundings and to the room (Fig. 9.9). Take the control volume to include the wall, and let the surfaces touch the environment on the outside and the air of the room inside; i.e., include in the control volume all three sources of entropy production. Now, the law of balance of entropy can be written in the form

$$\dot{S} = I_{Sa} + I_{S,room} \tag{9.38}$$

where we have assumed that solar radiation does not deliver any entropy. The currents and the rate of change are expressed by

$$I_{Sa} = -\frac{1}{T_a} h_a A\left(T - T_a\right)$$
$$I_{S,room} = -\frac{1}{T_{room}} h_{room} A\left(T - T_{room}\right) \tag{9.39}$$
$$\dot{S} = \frac{1}{T}\dot{E} = \frac{1}{T}\left(I_{Ea} + I_{E,room} + A\,a\mathcal{G}\right)$$

The last expression is a consequence of the balance of energy, which takes the form

$$\dot{E} = I_{Ea} + I_{E,room} + A\,a\mathcal{G} \tag{9.40}$$

Here, $A a\mathcal{G}$ is the product of absorptivity of the wall and solar irradiance. The problem is to find expressions for the heat transfer coefficients from the wall to the surroundings and the room, and one for the relation between energy (or entropy) and the temperature of the wall. If we treat the wall as spatially uniform, and if we take a simple model for the computation of the transfer coefficients, we get

$$\dot{E} = C\dot{T}$$
$$\frac{1}{h_a} = \frac{1}{h_{wall-air}} + \frac{d/2}{k_E} \tag{9.41}$$
$$\frac{1}{h_{room}} = \frac{1}{h_{wall-room}} + \frac{d/2}{k_E}$$

where *d* is the thickness of the wall. Heat is assumed to be transferred from the middle of the wall out into the environment or into the room. It turns out that the total entropy produced over a cycle of charging and discharging of the storage element has a minimum for a particular value of the thickness of the wall (Fig. 9.10). Not surprisingly, this value also coincides with the maximum of the entropy delivered to the room.

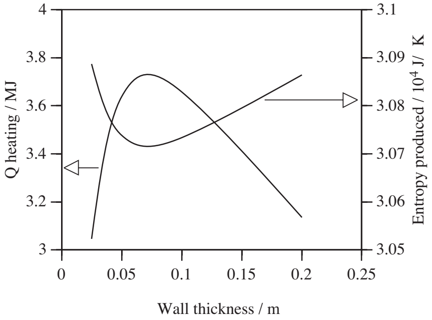

Figure 9.10: Results for the storage wall. The wall (T_{init} = 20°C) is charged for 8 hours, during which time it also loses heat to the surroundings (T_a = 0°C.) After charging, it is allowed to lose heat to the room (T_{room} = 20°C) and to the environment. The calculation is performed up to the time when the wall has again reached a temperature of 20°C.

9.6 ATMOSPHERE AND WINDS

The Earth's atmosphere provides for an interesting system whose operation can be understood partially with the help of rather simple models. The simplest and most famous of these probably are calculations of expected surface temperatures of a planet in the light of the Sun where the planet is treated as a uniform object in steady-state (see Example 7.12 in Chapter 7).

In this section, I will repeat the example by showing that the result is obtained not only by applying the balance of energy but also if we perform an analysis based on entropy and minimize the entropy production rate. (There has been one such example before where this approach could be applied successfully, namely, the calculation of the adiabatic flame temperature in Example 8.11, Chapter 8.) The model will then be extended by including an atmosphere—an absorbing and radiating layer above the surface. The same method of calculating the minimal entropy production rate will yield the solution of the model (the same solution one would also obtain by applying the balance of energy). This is the simplest possible model for explaining the greenhouse effect.

A still more interesting model treats the atmosphere as a heat engine—similar to the one discussed in Section 9.3—driving the winds on the planet.[9] Here we have a free parameter which is found by minimizing the total entropy production rate. The result is the expected power of the winds on our planet. Finally, the model will be combined with the one leading to a greenhouse effect. Interestingly, the numerical results are close to real values.

9.6.1 Surface Temperature of a Planet Without an Atmosphere

Imagine a planet in the light of the Sun. It receives radiation (of which it absorbs a fraction a_s) that is uniform over an area equal to the cross section of the planet. If we assume the surface to be perfectly conducting, its surface temperature can be taken to be uniform. This means that the planet—a sphere—radiates uniformly in all directions from its entire surface. This geometric effect—absorption over the cross section and emission over the entire surface—can be taken into account of we assume a uniform incoming irradiance for the entire planetary surface which is exactly one quarter of the actual irradiance of the Sun (see the factor 1/4 in Equ.(9.43)$_1$).

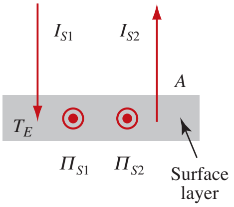

Figure 9.11: Entropy fluxes and entropy production rates for a surface layer of a body in the light of the Sun.

The model is one of a piece of surface having an area A (Fig. 9.11). There are two entropy fluxes, one incoming, one outgoing, and entropy production rates due to absorption and emission. In steady-state, the balance of entropy of the system reads[10]

$$0 = I_{S1} + I_{S2} + \Pi_{S1} + \Pi_{S2} \tag{9.42}$$

The entropy fluxes from the Sun—the part intercepted and absorbed—and from the warm planetary surface have been calculated before in Section 7.4.3:

$$\begin{aligned} I_{S1} &= \frac{1}{4} A \frac{4}{3} \frac{a_s G_{sc}}{T_s} \\ I_{S2} &= -A\sigma \frac{4}{3} T_E^3 \end{aligned} \tag{9.43}$$

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[9] This problem was first treated in a different manner by Gordon and Zarmi (1989). Their model is different and yields different values.

[10] Remember the discussion of fields and bodies, and entropy fluxes and entropy source rate in Section 7.1. If we want to be careful with concepts and terms, Equ.(9.42) applies to the system made up of surface layer plus radiation fields.

Entropy production due to absorption of sunlight and emission from the surface have been expressed in Section 7.4.3 as well:

$$\begin{aligned} \Pi_{S1} &= \left(\frac{3}{4}\frac{T_s}{T_E} - 1\right) I_{S1} \\ \Pi_{S2} &= -\frac{1}{4} I_{S2} \end{aligned} \tag{9.44}$$

If we add the contributions to entropy production in order to obtain the total irreversibility, insert the expressions for the entropy fluxes, and then determine the minimal entropy production rate, we have a condition for the unknown surface temperature T_E of the planet. The derivation proceeds as follows:

$$\Pi_S = \left(\frac{3}{4}\frac{T_s}{T_E} - 1\right) I_{S1} - \frac{1}{4} I_{S2} = \frac{1}{4} A \frac{a_s \mathcal{G}_{sc}}{T_E} - \frac{1}{4} A \frac{4}{3}\frac{a_s \mathcal{G}_{sc}}{T_s} + \frac{1}{4} A\sigma \frac{4}{3} T_E^3$$

$$\frac{d}{dT_E}\Pi_S = -\frac{1}{4} A a_s \mathcal{G}_{sc} \frac{1}{T_E^2} + A\sigma T_E^2$$

If the derivative of the entropy production rate with respect to the unknown temperature is set equal to zero, we obtain

$$T_E^4 = \frac{1}{4\sigma} a_s \mathcal{G}_{sc} \tag{9.45}$$

which is the same result as the one derived in Example 7.12. For $a_s = 0.7$ and $\mathcal{G}_{sc} = 1370\ \mathrm{W/m^2}$, the surface temperature of the model planet would be 255 K.

9.6.2 The Greenhouse Effect

Now imagine a layer of air above the ground (shown in the model of Fig. 9.11). The presence of this element—which we are going to model as a uniform body—changes the situation discussed above in several important ways (Fig. 9.12). To limit the details to be considered, assume the reflectance (albedo) of the planet to be due solely to the atmosphere. This means we assume the air (the clouds, mostly) reflects a part of the incoming radiation. Whatever is not reflected passes through (the atmosphere in our model does not absorb shortwave solar radiation). Also, the ground is understood to be a perfect absorber which means that it does not reflect either solar radiation or the long-wave back-radiation from the warm atmosphere.[11] The atmosphere absorbs only long-wave radiation from the ground and emits its own (long-wave) radiation both toward the ground and the sky. A part of the radiation from the warm ground is assumed to pass unhindered through the atmospheric layer.

Laws of balance. The laws of balance of entropy have to be formulated for the elements of our model. With $\Pi_{Sg} = \Pi_{S1} + \Pi_{S2} + \Pi_{S3}$, the steady state balance of entropy for the ground is

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[11] Remember that radiation from a gray body or surface that radiates and reflects can be treated by introducing the concept of radiosity (Section 7.4.4).

$$I_{S1} + I_{S3} + \Pi_{Sg} = I_{S2} \tag{9.46}$$

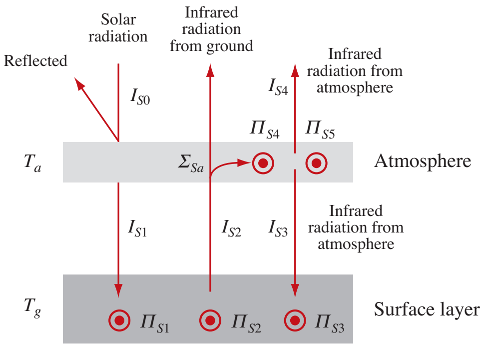

Figure 9.12: A model of a planet with an atmospheric layer. Planet (ground g) and atmosphere (a) are both treated as uniform bodies in steady-state. The atmosphere absorbs part of the (infrared) radiation from the ground and radiates toward the ground and the sky. The figure shows entropy flows and entropy production rates.

The symbols stand for the absolute values of the quantities involved. The total entropy production rate in the ground is the sum of three terms: one for the absorption of solar radiation, one for the absorption of the radiation from the atmosphere, and the third for the emission of radiation of the ground at temperature T_g. The law of balance for the atmosphere takes the form

$$\Sigma_{Sa} + \Pi_{Sa} = I_{S3} + I_{S4} \tag{9.47}$$

where Σ_{Sa} is the rate of absorption of entropy by the atmosphere, and Π_{Sa} is the sum of entropy production rates due to absorption and emission.

Constitutive relations. I_{S1} and I_{S2} are the same as in Equ.(9.43), and Π_{S1} and Π_{S2} are given by Equ.(9.44). Π_{S3} is new in this model and it is given by

$$\Pi_{S3} = \left(\frac{3}{4}\frac{T_a}{T_g} - 1\right) I_{S3} \tag{9.48}$$

The rate of absorption of entropy by the atmosphere, Σ_{Sa}, is a fraction of the entropy current I_{S2} (a realistic value for the absorptivity of the atmosphere is 0.87). The entropy currents from the atmosphere to the ground and to the sky are equal, and they are given by

$$I_{S2} = -Ae\sigma\frac{4}{3}T_a^3 \tag{9.49}$$

e is equal to the absorptivity of the atmosphere if this element is modeled as a gray body, so we set $e = 0.87$. Expressions for the entropy production rates in the atmosphere complete the model:

$$\begin{aligned} \Pi_{S4} &= \left(\frac{3}{4}\frac{T_g}{T_a} - 1\right)\Sigma_{Sa} \\ \Pi_{S5} &= 2\frac{1}{4}I_{S3} \end{aligned} \tag{9.50}$$

The factor 2 in the last equation is due to the fact that the atmosphere radiates up and down equally. If we use the same parameters as in the previous model and a value of $e = 0.87$ for the atmosphere, numerically solving the equations yields temperatures of 248 K for the atmosphere and 294.5 K for the ground. The latter value is a major correction of the result for a planet without an atmosphere (Section 9.6.1) but it is a little higher than the average temperature of the Earth which is about 288 K. We will get another correction of this value in the right direction by assuming that a part of the entropy radiated by the ground is used to drive the winds.

9.6.3 A Wind Engine

We can view the Earth's atmosphere as a simple heat engine powered by the Sun. The motive power of this engine drives the winds. Obviously, the processes involved are highly dissipative, and we might ask what the efficiency of the engine would be at maximum mechanical power or rather at minimal entropy production. As you will see, the results of a simple model of a heat engine at minimal irreversibility yields a good upper bound on the energy of the winds on the surface of the Earth.

As a first approximation, the winds are the result of differential heating of the surface air leading to giant cells of ascending and descending air. Let us model the entire atmosphere as moving as one big cell above a flat surface at temperature T_g (Fig. 9.13). To minimize any problems we shall only consider spatial and temporal averages. In other words, we shall model a spatially uniform engine working in a steady state.

We shall consider the air as the endoreversible heat engine (HE in Fig. 9.13). This engine receives entropy from the surface at an unknown temperature T_{aH}. Naturally, T_{aH} must be smaller than the temperature of the Earth if entropy is to be transferred from the ground to the air. A fraction of the entropy leaving the ground will be accepted through a transfer layer TL by the engine, which we consider to run ideally. The rest of the entropy absorbed by the surface will be radiated directly into space, which we assume to have a temperature T_o of 3 K. In other words we do not include the greenhouse effect in this first model of the winds.

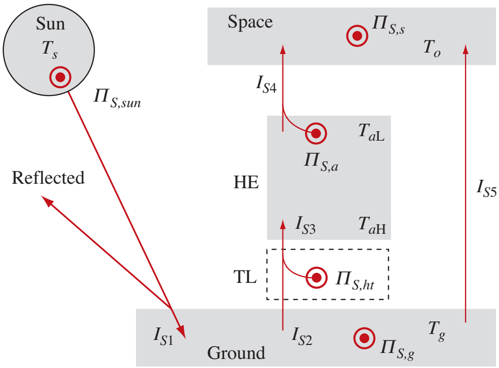

Figure 9.13: The surface of the Earth is heated by solar radiation. Part of the entropy is radiated back into space while the rest heats the air. As a result the air begins to rise and cool down. At high altitudes, the entropy absorbed is radiated into space whereupon the air descends back to the surface. In its simplest form this process constitutes a Carnot cycle releasing energy for a mechanical purpose. In our case, this is the generation of the winds.

The heated air will rise adiabatically, after which the entropy it received will be radiated away into space. The temperature of the air at higher altitudes where radiation into space takes place will be called T_{aL}. After this step the air will sink back down to the surface, again without exchanging any entropy. The model presented here is an endoreversible Carnot engine which is a relatively crude approximation of actual conditions. Nevertheless, we still can hope to obtain some interesting results.

While we have taken the model engine to work as an ideal Carnot heat engine, the entire system, which includes the radiative transfer of entropy, is dissipative. Emission of entropy from a body at higher temperature and absorption of it by a different body at lower temperature leads to the production of entropy, and so does entropy transfer from the ground to the air through the transfer layer TL (Fig. 9.13). It seems reasonable to assume that the entire system will maximize power output by minimizing the rate of production of entropy. Therefore we shall have to consider in detail the dissipation occurring as a result of transfer processes.

The system runs in steady-state mode. The laws of balance of entropy for Ground, transfer layer TL, and heat engine HE are

$$\begin{aligned} I_{S1} + \Pi_{S,g} &= I_{S2} + I_{S5} \\ I_{S2} + \Pi_{S,ht} &= I_{S3} \\ I_{S3} + \Pi_{S,a} &= I_{S4} \end{aligned} \qquad \textbf{(9.51)}$$

Of the five entropy currents that occur in the model shown in Fig. 9.13, four are given by independent expressions:

$$\begin{aligned} I_{S1} &= 0.25(1 - albedo)\left(\frac{R_s}{d}\right)^2 \frac{4}{3}\sigma T_s^3 \\ I_{S2} &= \frac{h}{T_g}\left(T_g - T_{a\mathrm{H}}\right) \\ I_{S4} &= \frac{4}{3}\sigma T_{a\mathrm{L}}^3 \\ I_{S5} &= \frac{4}{3}\sigma T_g^3 \end{aligned} \qquad \textbf{(9.52)}$$

The equations have been written for a surface area of 1 m^2. h is the heat transfer coefficient for the air moving over the ground (we choose a value of 20 W/(K·m^2)), and the albedo is equal to the reflectivity of the planet (0.30). R_s and d symbolize the radius of the Sun and the distance between Sun and Earth, respectively. Note that the last two of these equations assume that the ground and the air radiate as black bodies.

There are four entropy production rates that have to be taken into account (we can neglect entropy production at the surface of the Sun since this is constant and does not play a role when we search for the minimum of entropy production). The first three are part of our planet:

$$\begin{aligned} \Pi_{S,g} &= \left(\frac{3}{4}\frac{T_s}{T_g} - 1\right) I_{S1} + \frac{1}{4} I_{S5} \\ \Pi_{S,ht} &= \frac{1}{T_{a\mathrm{H}}}\left(T_g - T_{a\mathrm{H}}\right) I_{S2} \\ \Pi_{S,a} &= \frac{1}{4} I_{S4} \end{aligned} \qquad \textbf{(9.53)}$$

and the fourth is associated with outer space:

$$\Pi_{S,s} = \left(\frac{3}{4}\frac{T_{aL}}{T_o} - 1\right) I_{S4} + \left(\frac{3}{4}\frac{T_g}{T_o} - 1\right) I_{S5} \tag{9.54}$$

The first, third, and fourth expression have to do with radiation, the second is the result of dissipation in the transfer layer TL. The final condition is the one that lets us calculate the power of the heat engine HE:

$$\mathcal{P}_{\mathrm{HE}} = \left(T_{aH} - T_{aL}\right) I_{S3} \tag{9.55}$$

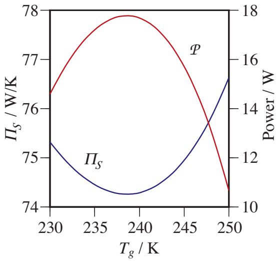

Figure 9.14: Entropy production rate and power of the wind engine as functions of surface temperature T_g.

This completes our model. When we try to solve the equations we realize that there is one unknown too many. We may take this to be the surface temperature of the Earth, T_g. When we vary the value of T_g, the total entropy production rate

$$\Pi_S = \Pi_{S,g} + \Pi_{S,ht} + \Pi_{S,a} + \Pi_{S,s} \tag{9.56}$$

changes (Fig. 9.14). Interestingly, it attains a minimum at a particular value of T_g which is close to 238 K (note that this value is smaller than the 255 K for the Earth without an atmosphere). The power of the wind engine turns out to be about 18 W per square meter. This number should be compared to the measured value which is about 7 W/m^2 averaged over time and surface of our planet. The result is very interesting in that it demonstrates that not just man-made engines may be designed according to the rule of minimal rate of entropy production. The Earth's atmosphere seems to follow the same rule quite naturally.

9.6.4 Combining Greenhouse and Wind Engine

The final step in the series of models discussed here is a combination of planet with greenhouse effect and wind engine (Fig. 9.15). The idea of this model is rather simple. Part of the entropy that will leave the ground is picked up conductively by the air and drives the wind engine. The part that is radiated directly into space in the model of Fig. 9.13 is now (mostly) absorbed by the air which is heated and now radiates up and down as in the model of Fig. 9.12. Basically, the equations presented in Section 9.6.2 and in Section 9.6.3 are combined and the minimum of the total entropy production rate is determined.

If we use the same parameters as before, the results of the model are 267 K for the surface temperature of the planet at minimal entropy production rate and a power of 26 W per square meter for the wind engine. The temperature moves in the right direction but the power of the winds is too high. Apart from the shortcomings of the model (considering all the effects that have been neglected) there is one factor that is very uncertain in the model as it stands. This is the emissivity of the air partaking in the wind engine. Here it has been given a value of 1. This is most certainly much too high. If we assume a relatively thin layer of the upper air in the wind engine to radiate into space (this is the entropy current I_{S4}), its absorptivity and therefore its emissivity should be considerably less than one. We can search for a value for the emissivity which yields a power of the winds of 7 W/m^2 (at minimal irreversibility); we obtain roughly 0.20 which does not seem totally unfounded. Moreover, the surface temperature turns out to be about 286 K which looks extremely good. However, we should not try to read too much into our simple models. They have been constructed as examples of how to do “thermal design” on an interesting natural system.

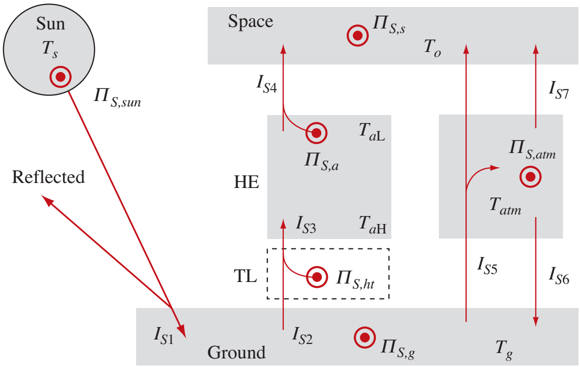

Figure 9.15: A combination of the models presented in Fig. 9.12 and Fig. 9.13. The entropy that does not go through the wind engine is (partially) absorbed by the atmosphere and radiated back to the ground and up into space.

EXERCISES AND PROBLEMS

1. Consider the flow of hot oil through a pipe. There are two sources of entropy production: friction and entropy loss (to the environment). Represent the two contributions to irreversibility as functions of the pipe’s radius in a graph. What is the radius of the pipe for which the total entropy production rate is minimal? What is the practical meaning of this result? Data: Viscosity: 0.20 Pa · s, Length: 1.0 m, Heat transfer coefficient: 10 W/(K · m^2), Volume flux: 0.010 m^3/s, $T_{oil} = 400$ K, $T_a = 300$ K, laminar flow.
2. Define the total loss of power in the case of hot oil flowing through a pipe in terms of energy loss due to heat loss and of friction. Calculate the radius of the pipe for which the loss is minimal. Why do you get a different result than the one calculated in Problem 1?
3. An endoreversible engine as presented in Section 9.2 is to be designed. It consists of the reversible Carnot engine and two heat exchangers serving the furnace and the cooler. (a) Prove that its power at maximum output can be written as

$$I_{E,mech} = \frac{(hA)_f}{1 + (hA)_f / (hA)_c} T \left[1 - \sqrt{\frac{T_0}{T}} \right]^2$$

where f and c refer to the furnace and the cooler, respectively. (b) If the power is maximized once more by optimally dimensioning relative sizes of the heat exchangers, we get

$$I_{E,mech} = \frac{1}{4} hA \cdot T \left[1 - \sqrt{\frac{T_0}{T}} \right]^2$$

where $hA = (hA)_f + (hA)_c$ is the total transfer coefficient multiplying the difference of temperatures. Derive this result. (c) Show that the optimized power of such an engine increases proportionally to $(T - T_0)^2/T$ for differences of temperatures which are not too large. This condition is quite applicable to today’s range of temperatures. What does this mean for the designer of a power plant?

4. The furnace of a large thermal power plant was designed to deliver energy at a rate of up to 2.0 GW at a temperature of 920 K. Cooling is done at an environmental temperature of 300 K. Model the engine as endoreversible. (a) How large is the current of entropy entering

the system? (b) What is the optimal mechanical power if heat leakage is responsible for a loss of 5% of the heating power? (c) What are the magnitudes of the rate of production of entropy and of the loss of available power? Are they related by the rule expressed in Chapter 4, Equ.(4.32)?

5. Derive a general expression for the second law efficiency of an endoreversible engine. Show that it is given by

$$\eta_{\mathrm{II}} = \frac{1}{1 + \sqrt{T_0/T}}$$

6. Model a refrigerator as an endoreversible engine. Its purpose is to pump heat out of the cold enclosure at a prescribed rate. The heat exchangers at the colder and at the warmer end have been dimensioned so that the temperature differences across them are roughly equal. You can now add a section of heat exchanger to only one of the existing exchangers. Which one do you choose? Assume the temperature differences across the heat exchangers to be small compared to the temperatures themselves and to the difference between the temperatures of the cold enclosure and the environment. The added section of heat exchanger is small compared to the existing ones.

7. Consider a solar furnace with a heat engine and a heat pump as in Problem 28 of Chapter 4. Water is to be heated at constant temperature T_w. The engines are supposed to be ideal Carnot engines. Entropy is supplied to and rejected from engines and reservoirs at constant temperatures. Assume the furnace to be an ideal absorber of solar radiation. The energy losses from the furnace to the environment are taken to be proportional to the difference of temperatures, with constant heat transfer coefficient h. (a) Derive the expression for the rate of production of entropy for the entire system. (b) How large should the temperature of the furnace be to minimize the production rate of entropy? (c) For which value of the temperature of the furnace will the power of the heat engine be a maximum? Why is this value different from the one computed in (b)? Should you try to minimize entropy production or to maximize power output of the heat engine? (d) Show that the maximum of the total heating power with which the body of water is being heated occurs at the same temperature of the furnace as that calculated for minimal entropy production.

8. An empty tank is filled with an externally heated fluid. Consider the irreversible processes due to fluid flow and heat loss from the tank to the environment. Assume fluid friction obeys the law of Hagen and Poiseuille. Heat loss from the tank should be proportional to how much hot fluid is in the tank. (a) Give qualitative reasons to show that there should be an optimal rate of charging of the tank. (b) Show that under these conditions, the optimal charging time should be proportional to the square root of the frictional resistance (as in Ohm's law, see Chapter 1), and inversely proportional to both the square root of the total heat transfer coefficient and the difference of temperatures between the hot fluid and the environment. (Assume the temperature decrease of the fluid in the tank due to cooling to be small; i.e., take the temperature of the heated fluid to remain constant.)

9. A tank containing a certain quantity of water at T_0 is charged with a stream of hot water at T_w while the same amount of water is withdrawn from an outlet. The mass flux is I_m. The water supplied to the tank instantaneously mixes with the fluid already there. There is heat loss to the surroundings at ambient temperature T_a. Are there conditions of minimal entropy production?

10. Solar panels heat water flowing through them. Assume we want to have hot water at a certain temperature (such as 60°C). Basically, there are three possibilities for getting 60°C water: (1) operate the solar collectors in such a way that they deliver water at precisely the desired temperature; (2) if they deliver colder water, heat it electrically to the desired temperature; (3) if the water from the collectors is too hot, mix in water having environmental temperature. Show that the first of these approaches is the most efficient from a thermal point of view. [Remark: Do the analysis for steady-state conditions. Radiation, temperatures, and mass flux are assumed to be constant.]

PART III

A DYNAMICAL THEORY OF HEAT

CHAPTER 10

THERMODYNAMICS OF SPATIALLY UNIFORM SYSTEMS

In this first chapter of Part III, I am going to develop an approach to the thermodynamics of spatially uniform fluid systems and processes which has been inspired by continuum thermodynamics.[1] It demonstrates the application of the laws of balance as the starting point of a description of nature. In contrast to the method used in Part II, it does not assume the form of the relationship between currents of entropy and of energy in heating and in cooling. Moreover, it does not follow the historical path of using power cycles for developing the theory, as is common in thermodynamics.

The following sections can be taken as a proof that the ideal gas temperature is the natural measure of the thermal potential. The method presented here will give you a firmer grounding in thermodynamics, and it will prepare you for the simple examples of continuum physics discussed in the following two chapters.

After developing the model of the dynamics of heat of a single viscous fluid, I will repeat the approach for fluids undergoing chemical change. We will start with phase changes and then move to proper reactions. The development should allow you to formulate equivalent models for other materials such as elastic bodies.

10.1 THERMODYNAMICS OF A SINGLE VISCOUS FLUID

I will introduce a generalized approach to thermodynamic theory here by applying it to a simple fluid, namely a single viscous uniform body that cannot change its phase. With the exception of viscosity, this is the example of a material we have encountered in Chapter 5 and again in Chapter 8 (for open systems) where we have assumed constitutive relations allowing only for ideal processes. We have seen that a theory of thermodynamics of such ideal fluids leads to the same relations known from thermostatics, as you can verify by comparison with standard texts on this subject. In other words, the ideal fluids considered so far attain the same properties during dynamical processes as in equilibrium states. The materials for which the theory holds obey such simple constitutive laws as to deliver results independent of the speed and other details of processes. Even though the derivation is one of a theory of dynamics, time apparently drops out of the equations in the end.

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[1] See I. Müller: *Thermodynamics* (1985).

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_11,

If you change the conditions just a little bit, for example by introducing a viscous pressure term, time appears explicitly in the results. This is what I would like to demonstrate on the following pages. The previous results will then be obtained in the limit of vanishing viscosity.

10.1.1 Viscous Pressure

First we should discuss how to include viscosity in the constitutive laws describing the behavior of the fluid. This will tell us something about the particular form the assumptions should take upon which we will base the following development.

Imagine a viscous fluid. Naturally, the effect of viscosity will be felt only as long as the fluid flows. In the case of a uniform body this means that its volume must change. As long as viscous effects are neglected, we would assume the pressure of the fluid to be expressed as a function of temperature and of volume; now, however, we will assume the pressure, which is equivalent to the momentum current density across a surface, to also depend upon the speed of the process:

$$P\left(V,T,\dot{V}\right) = P\big|_E\left(V,T\right) + a\dot{V} \tag{10.1}$$

$P|_E$ is the static pressure of the fluid, i.e., the value of the pressure attained when the volume does not change, or if viscosity is neglected. As you can see, the rate of change of the volume of the body is therefore included as one of the independent variables of the theory. This will have important consequences for the assumptions to be made regarding the behavior of the fluid.

10.1.2 Assumptions

We need to make a number of assumptions to develop a theory of thermodynamics of a particular type of material. Basically, the fundamental laws used so far, with the exception of the relation between currents of entropy and of energy in heating, and with Equ.(1) replacing a simpler form of the equation of state, will furnish the foundation. Naturally, leaving out one assumption calls for a replacement, unless it was an unnecessary one to begin with:

1. First, we have to agree on the independent variables of the theory. As before, they will be the volume and the temperature of the uniform fluid, which now will be joined by the rate of change of the volume. Therefore, entropy, energy, pressure, and other quantities will be functions of *V*, *T*, and *dV/dt:*

   $$S = S\left(V,T,\dot{V}\right) \quad , \quad E = E\left(V,T,\dot{V}\right) \quad , \quad P = P\left(V,T,\dot{V}\right) \quad , \quad \ldots$$

   This requirement carries over to quantities such as the entropy capacitance and the latent entropy.

2. While we do not take the relation between currents of entropy, currents of energy, and temperature for granted (i.e., we do not assume the important law $I_{E,th} = T\,I_S$, with T the ideal gas temperature, to hold), we accept a constitutive law for the flux of energy in heating which makes it proportional to the flux of entropy.[2] If we heat twice as fast, i.e., if we double the current of entropy, we also double the current

of energy associated with the heating:

$$I_{E,th} \propto I_S \tag{10.2}$$

We see that this is a particular constitutive assumption. The flux of energy associated with compression and expansion of the uniform fluid, on the other hand, is well known:

$$I_{E,comp} = -P\dot{V} \tag{10.3}$$

3. The additional assumption needed in place of knowledge of the full relation between the currents of entropy and of energy in heating can be furnished as follows. We introduce ideal walls separating different fluid systems.[3] Ideal walls are defined to be those which do not contribute to thermal processes; i.e., they do not produce entropy. This means that as part of the definition, the entropy flux across an ideal wall is continuous:

$$I_S(\mathrm{I}) = I_S(\mathrm{II}) \tag{10.4}$$

where the roman numerals refer to the fluids separated by the wall. As the actual assumption, we take for granted that two fluids separated by an ideal wall will have the same temperature at the wall:

$$T(\mathrm{I}) = T(\mathrm{II}) \tag{10.5}$$

Naturally, the flux of energy is continuous across this wall as well (remember the discussion in Section 4.8). Assuming the existence of such walls is necessary for the measurement of temperature to work the way we know it: one of the fluids separated by the wall would be the fluid of the thermometer, the other would be the body whose temperature we wish to measure. Only the fluids, not the wall separating them, may have an influence upon the temperatures (see Fig. 10.1).

4. With these preliminaries, we can state the laws of balance which we take to be valid in the current case. They are the expressions of balance of entropy (for the ther-

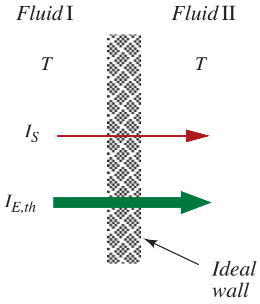

Figure 10.1: Two fluids of the same type are separated by an ideal wall. Across such a wall, entropy and energy flux are continuous. Also, it is assumed that the temperature is the same on both sides.

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[2] In continuum physics, we have Fourier's law for the entropy flux density for fluids such as those described by the Navier-Stokes-Fourier equations:

$$j_S = -\varphi(T,\rho)\frac{dT}{dx}$$

The same type of equation also applies to the thermal energy flux density:

$$j_{E,th} = -\beta(T,\rho)\frac{dT}{dx}$$

Hence, the requirement of proportionality between these fluxes is satisfied. (See Chapter 12 for a more detailed discussion.) We have previously assumed constitutive laws of heating of uniform fluids for which this requirement is fulfilled as well.

[3] For a discussion, see Müller (1985), p. 168–169. The assumption of the continuity of temperature at an ideal wall, Equ.(10.5), replaces other assumptions which are made in different approaches to thermodynamics.

mal process), and of momentum (for the mechanical process). Therefore, we postulate that

$$\begin{aligned} \dot{S} &= I_S + \Pi_S \\ \dot{p} &= I_p \end{aligned} \tag{10.6}$$

Obviously, we should include the effect of irreversibility as a consequence of the viscosity of the material. Since the fluids are basically at rest, the balance of momentum is trivial and will not be explicitly required any longer.

5. Processes also satisfy the requirement of the balance of energy, in addition to the laws of balance for the special processes taking place. Since the particular fluids under investigation allow for thermal and mechanical changes only, the equation of balance of energy takes the form

$$\dot{E} = I_{E,comp} + I_{E,th} \tag{10.7}$$

Remember that this law does not distinguish between different types of physical processes; that is the responsibility of the other laws of balance.

10.1.3 Consequences of the Energy Principle

The crucial point about processes undergone by physical systems is that in addition to the proper laws of balance, they always satisfy the energy principle, i.e., the law of balance of energy, as well. This requirement may be expressed as follows:

> *Physical processes obey the energy principle. If these processes are required to be thermal, they also satisfy the balance of entropy; the law is then said to be a restriction upon the processes. If the phenomena are also supposed to be mechanical, a second restriction applies to them, namely the law of balance of momentum. Each particular law of balance serves as a restriction upon the form the laws governing a process may take.*

Now, such restrictions can be taken into account using Lagrange multipliers;[4] both Equations $(10.6)_1$ and (10.7) are satisfied simultaneously if and only if[5]

$$\dot{E} - I_{E,comp} - I_{E,th} - \lambda^S\left[\dot{S} - I_S - \Pi_S\right] = 0 \tag{10.8}$$

(Remember that we do not have to explicitly take the law of balance of momentum into consideration here.) This is the starting point of one of the approaches developed in continuum thermodynamics, which for lack of a better name, is called *thermodynamics with Lagrange multipliers*. Equ.(10.8) is obtained by subtracting the entropy principle (multiplied by a Lagrange multiplier) from the law of balance of energy. Naturally, λ^S must have the dimension of temperature for the equation to be dimensionally correct.

The next steps consist of expressing the mechanical current of energy, which is a result of changes of volume, and determining the time derivatives of the energy and entropy functions. Since these quantities are functions of volume, temperature, and rate of change of volume, we can write Equ.(10.8) as follows:

$$
\begin{aligned}
&\frac{\partial E}{\partial V}\dot{V}+\frac{\partial E}{\partial T}\dot{T}+\frac{\partial E}{\partial \dot{V}}\ddot{V}+\left(P\big|_E+a\dot{V}\right)\dot{V}-I_{E,th}\\
&\qquad -\lambda^S\left[\frac{\partial S}{\partial V}\dot{V}+\frac{\partial S}{\partial T}\dot{T}+\frac{\partial S}{\partial \dot{V}}\ddot{V}-I_S-\mathit{\Pi}_S\right]=0
\end{aligned}
\qquad \textbf{(10.9)}
$$

To obtain this result, the derivatives of $E(V,T,dV/dt)$ and $S(V,T,dV/dt)$ have been written in terms of their partial derivatives, and the law for the mechanical (compressional) energy flux for uniform viscous fluids has been applied (remember Section 2.3.2 and Equ.(10.3)). If we combine terms which are explicitly linear in the time derivatives of the independent variables V, T, and dV/dt, Equ.(10.9) becomes

---

4. Lagrange multipliers are known from extremal problems. Assume that a function $f(x_1,x_2,x_3)$ is to be maximized under the additional assumption that the two relations $g_i(x_1,x_2,x_3) = 0$, $i = 1,2$, have to be satisfied. These requirements mean that the three total derivatives have to be zero:

$$
\begin{aligned}
\frac{\partial f}{\partial x_1}\dot{x}_1+\frac{\partial f}{\partial x_2}\dot{x}_2+\frac{\partial f}{\partial x_3}\dot{x}_3&=0\\
\frac{\partial g_1}{\partial x_1}\dot{x}_1+\frac{\partial g_1}{\partial x_2}\dot{x}_2+\frac{\partial g_1}{\partial x_3}\dot{x}_3&=0\\
\frac{\partial g_2}{\partial x_1}\dot{x}_1+\frac{\partial g_2}{\partial x_2}\dot{x}_2+\frac{\partial g_2}{\partial x_3}\dot{x}_3&=0
\end{aligned}
$$

The dot denotes a derivative with respect to some parameter. The restrictions are taken into consideration using Lagrange multipliers λ^1 and λ^2. The last two equations are each multiplied by one of the factors and then added to the first. This leads to

$$
\begin{aligned}
&\left[\frac{\partial f}{\partial x_1}+\lambda^1\frac{\partial g_1}{\partial x_1}+\lambda^2\frac{\partial g_2}{\partial x_1}\right]\dot{x}_1+\left[\frac{\partial f}{\partial x_2}+\lambda^1\frac{\partial g_1}{\partial x_2}+\lambda^2\frac{\partial g_2}{\partial x_2}\right]\dot{x}_2\\
&\qquad\qquad+\left[\frac{\partial f}{\partial x_3}+\lambda^1\frac{\partial g_1}{\partial x_3}+\lambda^2\frac{\partial g_2}{\partial x_3}\right]\dot{x}_3=0
\end{aligned}
$$

The restrictions introduced here mean that two of the unknown functions x_i could be expressed in terms of the third. One may therefore chose the Lagrange multipliers such that the first two terms in brackets are equal to zero. (These are equations for the two unknowns.) As a result, the third term in brackets must also be equal zero. We therefore obtain three new relations

$$
\begin{aligned}
\frac{\partial f}{\partial x_1}+\lambda^1\frac{\partial g_1}{\partial x_1}+\lambda^2\frac{\partial g_2}{\partial x_1}&=0\\
\frac{\partial f}{\partial x_2}+\lambda^1\frac{\partial g_1}{\partial x_2}+\lambda^2\frac{\partial g_2}{\partial x_2}&=0\\
\frac{\partial f}{\partial x_3}+\lambda^1\frac{\partial g_1}{\partial x_3}+\lambda^2\frac{\partial g_2}{\partial x_3}&=0
\end{aligned}
$$

which have to be satisfied together with the two restrictions. In summary, we have five equations for the unknowns x_i, and for the Lagrange multipliers λ^i. Because of the similarity of their approach with the classical method of Lagrange multipliers, Liu and Müller (see Müller, 1985) have chosen to call the λ's Lagrange multipliers.

$$\begin{aligned}&\left[\frac{\partial E}{\partial V}-\lambda^{s}\frac{\partial S}{\partial V}+P\big|_{E}\right]\dot{V}+\left[\frac{\partial E}{\partial T}-\lambda^{s}\frac{\partial S}{\partial T}\right]\dot{T}\\&\qquad+\left[\frac{\partial E}{\partial \dot{V}}-\lambda^{S}\frac{\partial S}{\partial \dot{V}}\right]\ddot{V}-I_{E,th}+\lambda^{S}I_{S}+a\dot{V}^{2}+\lambda^{S}\Pi_{S}=0\end{aligned} \tag{10.10}$$

This equation must hold for all imaginable processes; i.e., it must be satisfied for all values of the derivatives of the independent variables. Assume this to be the case for a set of such values. Now change one of them just a little bit: in general, Equ.(10.9) will not be satisfied anymore unless the factor multiplying this derivative is set equal to zero. Since this reasoning applies to all terms explicitly involving the derivatives, the following three equations must hold:

$$\begin{aligned}&\frac{\partial E}{\partial V}-\lambda^{S}\frac{\partial S}{\partial V}+P\big|_{E}=0\\&\frac{\partial E}{\partial T}-\lambda^{S}\frac{\partial S}{\partial T}=0\\&\frac{\partial E}{\partial \dot{V}}-\lambda^{S}\frac{\partial S}{\partial \dot{V}}=0\end{aligned} \tag{10.11}$$

This leaves us with the residual equation

$$-I_{E,th}+\lambda^{S}I_{S}+a\dot{V}^{2}+\lambda^{S}\Pi_{S}=0$$

We can say a couple of things about this equation. For one, the assumption that the fluxes of entropy and of energy in heating are proportional requires

$$I_{E,th}=\lambda^{S}I_{S} \tag{10.12}$$

which at the same time means that

$$\Pi_{S}=-\frac{a}{\lambda^{S}}\dot{V}^{2} \tag{10.13}$$

Obviously, the production of entropy is a direct consequence of the viscosity of the fluid. Clearly, *a* must be negative or zero.

10.1.4 Determination of the Lagrange Multiplier

Equations (10.11) through (10.13) are the preliminary results of our theory. If we manage to determine the multiplier λ^S in terms of physical quantities, we will have the basis for deriving all desired results about the particular material investigated.

There are still a couple of assumptions we have not used so far. First, we shall make use of the idea regarding ideal walls. Imagine two uniform ideal fluids (I and II) to be

---

5. This proof, and the proof of the equivalence of these expressions to the requirement presented in Equ.(10.11), has been given by Liu (1972) for the general case. See also Müller (1985, p. 170).

separated by an ideal wall that only lets entropy and energy pass (see Fig. 10.1). Equ.(10.12) holds for both fluids which means that

$$I_{E,th}(\mathrm{I}) - \lambda^S\left(V_\mathrm{I}, T_\mathrm{I}, \dot{V}_\mathrm{I}\right) I_S(\mathrm{I}) = I_{E,th}(\mathrm{II}) - \lambda^S\left(V_\mathrm{II}, T_\mathrm{II}, \dot{V}_\mathrm{II}\right) I_S(\mathrm{II}) \tag{10.14}$$

Since both fluxes and the temperature are continuous across the wall, this condition reduces to

$$\lambda^S\left(V_\mathrm{I}, T, \dot{V}_\mathrm{I}\right) = \lambda^S\left(V_\mathrm{II}, T, \dot{V}_\mathrm{II}\right) \tag{10.15}$$

The volume and the rate of change of the volume of the two fluids are independent and can be given any values; this means that the Lagrange multiplier may only be a function of temperature, and not of the other two independent variables. We have

$$\lambda^S = \lambda^S(T) \tag{10.16}$$

The multiplier is a universal function of temperature, the same for all fluids of the type considered here.

We have to perform one more step before we can apply the results to the ideal gas and find the Lagrange multiplier. Since λ^S only depends upon the temperature of the fluid, Equ.$(10.11)_{(3)}$ reduces to

$$\frac{\partial}{\partial \dot{V}}\left(E - \lambda^S S\right) = 0$$

which means that $E - \lambda^S S$ is independent of dV/dt. Next, Equ.$(10.11)_{(2)}$ is transformed into

$$\frac{\partial}{\partial T}\left(E - \lambda^S S\right) = -S\frac{d\lambda^S}{dT}$$

This means that both the entropy and the energy of the fluid must be independent of the rate of change of the volume, and Equ.$(10.11)_{(3)}$ can be dropped from the list of results. These are strong restrictions upon the behavior of the material. We can say that

$$\begin{aligned} S &= S(V,T) \\ E &= E(V,T) \end{aligned} \tag{10.17}$$

Now we are ready to determine the Lagrange multiplier. For the moment, we will set the parameter a, which describes the effects of viscosity in Equ.(10.1), equal to zero. Since we have additional constitutive information about the ideal gas, let us apply the results to this body. We solve the first two parts in Equ.(10.11) for the derivatives of the energy function, and take the derivative with respect to the other independent variable:

$$\begin{aligned} \frac{\partial}{\partial T}\left(\frac{\partial E}{\partial V}\right) &= \frac{\partial}{\partial T}\left(\lambda^S \frac{\partial S}{\partial V} - P\big|_E\right) = \lambda^S \frac{\partial^2 S}{\partial V \partial T} + \frac{d\lambda^S}{dT}\frac{\partial S}{\partial V} - \frac{\partial P\big|_E}{\partial T} \\ \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial T}\right) &= \frac{\partial}{\partial V}\left(\lambda^S \frac{\partial S}{\partial T}\right) = \lambda^S \frac{\partial^2 S}{\partial T \partial V} \end{aligned}$$

If the functions are assumed to be sufficiently smooth, the mixed derivatives must be equal. Therefore, we obtain the condition

$$\frac{d\lambda^S}{dT}\frac{\partial S}{\partial V} = \frac{\partial P|_E}{\partial T}$$

or

$$\frac{d\lambda^S}{dT}\left(\frac{\partial E}{\partial V} + P|_E\right)\frac{1}{\lambda^S} = \frac{\partial P|_E}{\partial T}$$

This finally leads to

$$\frac{1}{\lambda^S}\frac{d\lambda^S}{dT} = \frac{\partial P|_E / \partial T}{\partial E/\partial V + P|_E} \tag{10.18}$$

This still holds for all fluids. In the case of the ideal gas, however, the special properties show that the right-hand side of Equ.(10.18) is equal to the inverse of the ideal gas temperature. Remember that the energy of the ideal gas depends only upon temperature:

$$\frac{1}{\lambda^S}\frac{d\lambda^S}{dT} = \frac{1}{T} \tag{10.19}$$

Integration of this result shows that the unknown Lagrange multiplier is the ideal gas temperature:

$$\lambda^S = T \tag{10.20}$$

In other words, the ideal gas temperature takes the role of the thermal potential. This concludes the proof of the relation between currents of entropy and of energy in heating of uniform fluids. Considering that we allow for irreversibility, the result is even more interesting than the equivalent statement which is traditionally derived for ideal fluids by analyzing cyclic processes (see the Interlude of the First Edition).

10.1.5 Results for Uniform Viscous Fluids

Now that the main unknown factor of the theory has been determined, we can collect the results and derive some more important expressions. First, the fluxes of entropy and of energy in heating are related by

$$I_{E,th} = T\, I_S \tag{10.21}$$

Second, the rate of production of entropy as a consequence of viscous pressure is

$$\Pi_S = -\frac{a}{T}\dot{V}^2 \tag{10.22}$$

Since Π_S cannot be negative, we conclude that the parameter a in the law of viscous pressure cannot take positive values:

$$\Pi_S \geq 0 \quad \Rightarrow \quad a \leq 0 \tag{10.23}$$

Furthermore, the properties of the fluids are such that the partial derivatives of energy and of entropy are related by

$$\begin{aligned} \frac{\partial E(V,T)}{\partial V} &= T\,\frac{\partial S(V,T)}{\partial V} - P\big|_E(V,T) \\ \frac{\partial E(V,T)}{\partial T} &= T\,\frac{\partial S(V,T)}{\partial T} \end{aligned} \tag{10.24}$$

This is a consequence of Equ.(10.11). This result can be used to derive the Gibbs fundamental form of the fluid. Since the time derivative of the energy is composed of partial derivatives, according to

$$\dot{E} = \frac{\partial E(V,T)}{\partial V}\dot{V} + \frac{\partial E(V,T)}{\partial T}\dot{T}$$

this quantity can be expressed using Equ.(10.24) to yield

$$\dot{E} = T\,\dot{S} - P\big|_E\,\dot{V} \tag{10.25}$$

Finally, if we introduce the entropy capacitance and the latent entropy; i.e., if we write

$$\begin{aligned} K_V &= \frac{\partial S(V,T)}{\partial T} \\ \Lambda_V &= \frac{\partial S(V,T)}{\partial V} \end{aligned} \tag{10.26}$$

we see that the flux of entropy in heating can be expressed as follows:

$$I_S = \Lambda_V \dot{V} + K_V \dot{T} + \frac{a}{T}\dot{V}^2 \tag{10.27}$$

Obviously, in the case of viscous fluids, heating depends upon the speed of the process; in other words, it is no longer reversible. If you calculate processes undergone by the fluids described in this section, time will appear explicitly in the equations; we will have standard initial value problems that are absent from traditional thermodynamics.

The results we have come across before in Chapter 5 can be derived as the limit of the present theory for vanishing viscosity: if you set $a = 0$, you will obtain the previous results. Aside from the inclusion of irreversibility, the new approach taken to thermodynamics is the most important aspect of this section; in particular, it demonstrates how we can derive the forms of potentials, such as the thermal potential which relates fluxes of entropy and of energy. Remember that historically, the route via the properties of heat engines was chosen. Today, we trust the law of balance of entropy as a general expression of the second law of thermodynamics; therefore, the development presented here seems to flow naturally from what we have learned about thermal processes. Moreover, note how time appears naturally in our relations: we have standard initial value problems to solve.

10.2 IDEAL FLUIDS WITH PHASE TRANSFORMATIONS

Consider a fluid composed of two phases of the same substance (Fig. 10.2). Both phases are assumed to have the same temperature and pressure. Basically, this sounds like the prescription for two unrelated, non-interacting fluids of the kind described in the previous section (if you disregard viscosity). However, in this case, the parts of the fluid are supposed to interact through a change of phase: one component can disappear while the amount of the other phase increases.

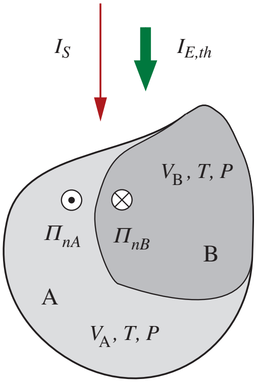

Figure 10.2: A system composed of two phases of the same fluid is heated. In addition to changes of volume and temperature, this case includes changes of amount of substance of the parts A and B. (When A loses an amount of substance, B gains just that much.) Temperature and pressure of the parts are assumed to be the same.

10.2.1 Assumptions

The assumptions that will be made in the course of the following derivation are mostly the same as those introduced above in Section 10.1. In particular, we are again dealing with ideal fluids and processes which do not produce entropy. Experience tells us that fluxes of entropy are reversed upon reversal of the changes undergone by the two phase fluids in chemical equilibrium shown in Fig. 10.2. Therefore, the equation of balance of entropy looks like the one used above:

$$\dot{S} = I_S \tag{10.28}$$

where the entropy of the system is now the sum of the entropies of the two phases A and B:

$$S(V,T,n) = S_A(V_A,T,n_A) + S_B(V_B,T,n_B) \tag{10.29}$$

Note that in the current case, the independent variables include the amounts of substance of the components.

Currents of entropy and of energy in heating are again taken to be proportional, as in Equ.(10.2), and we take the existence of ideal walls for granted.

We now have to add equations of balance for the two species A and B. There is no flow of any substance across system boundaries, but both A and B can undergo phase changes, leading to the production or destruction of the species. Therefore, the equations of balance read

$$\begin{aligned} \dot{n}_A &= \Pi_{nA} \\ \dot{n}_B &= \Pi_{nB} \end{aligned} \tag{10.30}$$

(Neglecting transports of the substances across the system boundary in Fig. 10.2 is of no fundamental significance.) Since the chemical reactions taking place are of a very special nature—when a unit of one phase disappears, exactly one unit of the other phase is produced—the rates of production and destruction are related by

$$\Pi_{nA} + \Pi_{nB} = 0 \tag{10.31}$$

Except for the balance of momentum, which, again, is trivial and does not have to be considered separately, these are the laws of balance of the processes taking place in the two phase fluids discussed here. As always, the processes also must satisfy the energy principle. The energy of the system can be changed only by energy flows due to heating or cooling and compression or expansion.

10.2.2 Consequences of the Balance of Energy

Even though we have extended the nature of the fluids under investigation, the law of balance of energy looks just like it did in the case of the single phase fluid. Since, with the exception of energy, the only physical quantities exchanged across the boundary of the system are entropy and momentum, the only energy currents are the thermal and the mechanical ones; the latter is related to compression or expansion:

$$\dot{E}_{\mathrm{A}} + \dot{E}_{\mathrm{B}} - I_{E,comp} - I_{E,th} = 0 \tag{10.32}$$

The expression for the exchange of energy in the compressional process is the same one used for the power of non-viscous uniform fluids. This time, however, we can write it with the volumes of both components in mind:

$$I_{E,comp} = -P\left(\dot{V}_{\mathrm{A}} + \dot{V}_{\mathrm{B}}\right) \tag{10.33}$$

The method of taking the balance of energy into account simultaneously with the balance of all other relevant quantities, once more requires the introduction of Lagrange multipliers. There is one such multiplier for every basic law of balance that is added to the list, including the energy principle. In our case, this means that we have to introduce three such factors, which we label λ^S, $\lambda^{n\mathrm{A}}$, and $\lambda^{n\mathrm{B}}$, respectively. The relation to be satisfied then takes the form:

$$\begin{aligned}&\dot{E}_{\mathrm{A}} + \dot{E}_{\mathrm{B}} + P\left(\dot{V}_{\mathrm{A}} + \dot{V}_{\mathrm{B}}\right) - I_{E,th}\\ &\quad - \lambda^S\left[\dot{S}_{\mathrm{A}} + \dot{S}_{\mathrm{B}} - I_S\right] - \lambda^{n\mathrm{A}}\left[\dot{n}_{\mathrm{A}} - \Pi_{n\mathrm{A}}\right] - \lambda^{n\mathrm{B}}\left[\dot{n}_{\mathrm{B}} - \Pi_{n\mathrm{B}}\right] = 0\end{aligned} \tag{10.34}$$

The following steps in evaluating the consequences of the energy principle are similar to those in the case of the single phase fluid. However, they involve some more algebra. First, we introduce the derivatives of the energy and the entropy with respect to the independent variables. After collecting the terms that are explicitly linear in the time derivatives of these independent variables, we obtain

$$\begin{aligned}&\left[\frac{\partial E_{\mathrm{A}}}{\partial V_{\mathrm{A}}} - \lambda^S\frac{\partial S_{\mathrm{A}}}{\partial V_{\mathrm{A}}} + P\right]\dot{V}_{\mathrm{A}} + \left[\frac{\partial E_{\mathrm{B}}}{\partial V_{\mathrm{B}}} - \lambda^S\frac{\partial S_{\mathrm{B}}}{\partial V_{\mathrm{B}}} + P\right]\dot{V}_{\mathrm{B}} + \left[\frac{\partial E_{\mathrm{A}}}{\partial T} - \lambda^S\frac{\partial S_{\mathrm{A}}}{\partial T}\right]\dot{T}\\ &\left[\frac{\partial E_{\mathrm{B}}}{\partial T} - \lambda^S\frac{\partial S_{\mathrm{B}}}{\partial T}\right]\dot{T} + \left[\frac{\partial E_{\mathrm{A}}}{\partial n_{\mathrm{A}}} - \lambda^S\frac{\partial S_{\mathrm{A}}}{\partial n_{\mathrm{A}}} - \lambda^{n\mathrm{A}}\right]\dot{n}_{\mathrm{A}} + \left[\frac{\partial E_{\mathrm{B}}}{\partial n_{\mathrm{B}}} - \lambda^S\frac{\partial S_{\mathrm{B}}}{\partial n_{\mathrm{B}}} - \lambda^{n\mathrm{B}}\right]\dot{n}_{\mathrm{B}}\\ &-\left[I_{E,th} - \lambda^S I_S\right] - \left[\lambda^{n\mathrm{A}}\Pi_{n\mathrm{A}} + \lambda^{n\mathrm{B}}\Pi_{n\mathrm{B}}\right] = 0\end{aligned}$$

The same arguments that led to Equations (10.11) and (10.12) also apply here. Starting with the second one, the fluxes of entropy and of energy will be proportional if

$$I_{E,th} = \lambda^S I_S \tag{10.35}$$

For the remainder of the equation, we can say that it has to be satisfied for all possible values of the rates of change of the independent variables. Since this requirement can easily be violated unless all factors are identically zero, we end up with the following relations:

$$\begin{aligned}
&\frac{\partial E_{\mathrm{A}}}{\partial V_{\mathrm{A}}} - \lambda^S \frac{\partial S_{\mathrm{A}}}{\partial V_{\mathrm{A}}} + P = 0 \\
&\frac{\partial E_{\mathrm{B}}}{\partial V_{\mathrm{B}}} - \lambda^S \frac{\partial S_{\mathrm{B}}}{\partial V_{\mathrm{B}}} + P = 0 \\
&\frac{\partial E_{\mathrm{A}}}{\partial T} - \lambda^S \frac{\partial S_{\mathrm{A}}}{\partial T} = 0 \\
&\frac{\partial E_{\mathrm{B}}}{\partial T} - \lambda^S \frac{\partial S_{\mathrm{B}}}{\partial T} = 0 \\
&\frac{\partial E_{\mathrm{A}}}{\partial n_{\mathrm{A}}} - \lambda^S \frac{\partial S_{\mathrm{A}}}{\partial n_{\mathrm{A}}} - \lambda^{n\mathrm{A}} = 0 \\
&\frac{\partial E_{\mathrm{B}}}{\partial n_{\mathrm{B}}} - \lambda^S \frac{\partial S_{\mathrm{B}}}{\partial n_{\mathrm{B}}} - \lambda^{n\mathrm{B}} = 0
\end{aligned} \tag{10.36}$$

and, for the production rates of the species:

$$\lambda^{n\mathrm{A}} \Pi_{n\mathrm{A}} + \lambda^{n\mathrm{B}} \Pi_{n\mathrm{B}} = 0 \tag{10.37}$$

This last relation will prove to be important when we interpret the meaning of the Lagrange multipliers that go with the species A and B. For now, we will use the reasoning presented when the Lagrange multiplier λ^S was determined. We start with a single-phase fluid for which the result of the previous section applies: λ^S is equal to the temperature. Then, a fluid (II) of this type is brought in contact with the two-phase fluid (I) via an ideal wall. Again, the argument which led to Equ.(10.14) is used; here it means that

$$\lambda^S(\mathrm{II}) = \lambda^S(\mathrm{I}) = T \tag{10.38}$$

All that remains to be done is to determine the multipliers λ^{nA} and λ^{nB}.

10.2.3 The Chemical Potential of Pure Fluids

Take a closer look at Equ.(10.37). If we combine it with the relation between the production rates, i.e., with Equ.(10.31), we see that the Lagrange multipliers of the two phases of the fluid must be equal:

$$\left(\lambda^{n\mathrm{A}} - \lambda^{n\mathrm{B}}\right)\Pi_{n\mathrm{A}} = 0 \quad \Rightarrow \quad \lambda^{n\mathrm{A}} = \lambda^{n\mathrm{B}} \tag{10.39}$$

Since the phases are in chemical equilibrium, it makes sense to interpret the as yet unknown factors as the chemical potentials of the fluid:

$$\lambda^{n\mathrm{A}} = \mu_{\mathrm{A}} \quad , \quad \lambda^{n\mathrm{B}} = \mu_{\mathrm{B}} \tag{10.40}$$

The rest of the equations derived above provide a means of relating the chemical potentials to other variables of the fluids. By introducing the Lagrange multipliers into the intermediate results, we obtain the laws that govern the behavior of pure fluids that may undergo phase transformations. First, the fluxes of entropy and of energy in heating must be related by the ideal gas temperature:

$$I_{E,th} = T\, I_S \tag{10.41}$$

Then, the partial derivatives of the energy and the entropy functions satisfy the relations presented in Equ.(10.36). For each of the phases, we may now write

$$\begin{aligned}
\frac{\partial E(V,T,n)}{\partial V} &= T\,\frac{\partial S(V,T,n)}{\partial V} - P(V,T,n)\\
\frac{\partial E(V,T,n)}{\partial T} &= T\,\frac{\partial S(V,T,n)}{\partial T}\\
\frac{\partial E(V,T,n)}{\partial n} &= T\,\frac{\partial S(V,T,n)}{\partial n} + \mu(V,T,n)
\end{aligned} \tag{10.42}$$

10.2.4 The Gibbs Fundamental Form and the Chemical Potential

Since the energy is a function of volume, temperature, and amount of substance, its time derivative is

$$\dot{E} = \frac{\partial E(V,T,n)}{\partial V}\dot{V} + \frac{\partial E(V,T,n)}{\partial T}\dot{T} + \frac{\partial E(V,T,n)}{\partial n}\dot{n}$$

Introducing the laws derived in Equ.(10.42) and collecting terms leads to the *Gibbs fundamental form* for fluids whose amount of substance may change:

$$\dot{E} = T\,\dot{S} - P\dot{V} + \mu\dot{n} \tag{10.43}$$

This is an extension of the form used for single-phase fluids. Again, there is one such relation for each of the phases. Now, we are ready to derive the relationship between the chemical potential and other variables of the fluid. We write each of the extensive quantities in Equ.(10.43) as the product of its density and the volume:

$$\frac{d}{dt}(\rho_E V) - T\,\frac{d}{dt}(\rho_S V) + P\frac{d}{dt}V - \mu\frac{d}{dt}(\rho_n V) = 0$$

Taking the derivatives leads to

$$[\rho_E - T\rho_S + P - \mu\rho_n]\dot{V} + [\dot{\rho}_E - T\dot{\rho}_S - \mu\dot{\rho}_n]V = 0$$

Since this relation must be satisfied for all possible (independent) values of the volume and its time derivative, both factors in brackets must be identically zero. Otherwise, the equation could be violated. The result of these considerations are the Gibbs fundamental form written in terms of the densities, and the relations between energy, entropy, density, and chemical potential:

$$\dot{\rho}_E = T\dot{\rho}_S + \mu\dot{\rho}_n \tag{10.44}$$

and

$$\bar{e} = T\,\bar{s} - P\bar{v} + \mu \tag{10.45}$$

The last formula has been rewritten by using molar quantities (see Equ.(8.46)).

10.2.5 Temperature and Pressure Dependence of the Chemical Potential

We have made extensive use of the dependence of the chemical potential upon temperature and pressure in the course of the applications presented in the previous sections. There, the proof was performed for special cases, but now we are in a position to deliver a general derivation.

In the development of the theory we started with temperature, volume, and amount of substance as the independent variables. With the Gibbs fundamental form, on the other hand, energy, temperature, pressure, and the chemical potential are variables of entropy, volume, and amount of substance. Other forms of Equ.(10.43) are based on other sets of independent variables. We need the set that includes temperature and pressure in addition to amount of substance. This transformation is facilitated using the definition of the *Gibbs free energy* function *G*:

$$G = E + PV - TS \tag{10.46}$$

The time derivative of this quantity is equal to

$$\dot{G} = \dot{E} + P\dot{V} + \dot{P}V - T\dot{S} - \dot{T}S$$

Using Equ.(10.43), this can be written

$$\dot{G} = V\dot{P} - S\dot{T} + \mu\dot{n} \tag{10.47}$$

which is an alternative fundamental form having independent variables *P*, *T*, and *n*. According to Equ.(10.47), the partial derivatives of *G*(*P,T,n*) are equal to the volume, the entropy, and the chemical potential, respectively:

$$\frac{\partial G(P,T,n)}{\partial P} = V(P,T,n) = n\overline{v}(P,T,n) \tag{10.48}$$

$$\frac{\partial G(P,T,n)}{\partial T} = -S(P,T,n) = -n\overline{s}(P,T,n) \tag{10.49}$$

$$\frac{\partial G(P,T,n)}{\partial n} = \mu(P,T,n) \tag{10.50}$$

Taking the derivative of Equ.(10.48) with respect to amount of substance, the derivative of Equ.(10.50) with respect to pressure, and equating the mixed derivatives

$$\frac{\partial}{\partial n}\frac{\partial G(P,T,n)}{\partial P} = \overline{v}(P,T)$$
$$\frac{\partial}{\partial P}\frac{\partial G(P,T,n)}{\partial n} = \frac{\partial \mu(P,T,n)}{\partial P}$$

we obtain the first of the desired results:

$$\frac{\partial \mu(P,T,n)}{\partial P} = \overline{v}(P,T) \tag{10.51}$$

The second one is derived in just the same way:

$$\frac{\partial \mu(P,T,n)}{\partial T} = -\bar{s}(P,T) \tag{10.52}$$

These are the relations we used above. They are an example of the restrictions put upon the multitude of quantities used for the description of phenomena; theory limits the number of independent functions which might have to be measured in the lab if property data are required (see Chapter 15).

10.2.6 The Clapeyron Equation

In Chapter 15, we will discuss in much more detail the fact that for phase changes, pressure and temperature are related directly. This is a consequence of the equality of the chemical potentials of both phases at the transition:

$$\mu_{\mathrm{I}}(P,T) = \mu_{\mathrm{II}}(P,T) \tag{10.53}$$

Since this holds for all values of the temperature, the derivative of the difference of the potentials with respect to *T* must be zero:

$$\frac{d(\mu_{\mathrm{II}} - \mu_{\mathrm{I}})}{dT} = 0 \tag{10.54}$$

Performing the differentiation leads to

$$\frac{\partial \mu_{\mathrm{II}}}{\partial T} + \frac{\partial \mu_{\mathrm{II}}}{\partial P}\frac{dP}{dT} - \left(\frac{\partial \mu_{\mathrm{I}}}{\partial T} + \frac{\partial \mu_{\mathrm{I}}}{\partial P}\frac{dP}{dT}\right) = 0$$

We can introduce the temperature and pressure dependence of the chemical potentials according to Equations (10.51) and (10.52), and obtain the Clapeyron equation:

$$-\bar{s}_{\mathrm{II}} + \bar{s}_{\mathrm{I}} + \left[\bar{v}_{\mathrm{II}} - \bar{v}_{\mathrm{I}}\right]\frac{dP}{dT} = 0 \tag{10.55}$$

In Chapter 15, we will make use of this result in the derivation of vapor pressure.

10.3 REACTION IN UNIFORM MIXTURES OF FLUIDS

Let us now treat the special case of reactions occurring in a closed system (no flow). A fluid is composed of several species which may react; it may exchange heat, and it is deformable. Still, we will treat the system as a uniform, non-viscous chunk of matter. The effects of motion will be neglected.

Again, we have to consider the proper expressions of balance which hold for entropy and amount of substance. Since we have *N* different species, we arrive at

$$\begin{aligned} &\dot{S} - I_S = \Pi_S \\ &\dot{n}_1 = \Pi_{n1} \quad , \quad \ldots \quad , \quad \dot{n}_N = \Pi_{nN} \end{aligned} \tag{10.56}$$

While we do not allow for convective currents in our model, we can no longer exclude the possibility of entropy being generated; indeed, we know that this is precisely what happens in reacting fluids that cannot undergo other processes; we therefore have an entropy production rate in the balance of entropy. As far as chemical substances are concerned, there is an equation of balance for the amount of substance of each of the species present.

Energy may be exchanged with the surroundings as a consequence of heating and of deformation. Therefore, we have an equation of balance of energy with two terms describing exchange, namely:

$$\dot{E} = I_{E,comp} + I_{E,th} \tag{10.57}$$

For the non-viscous, uniform fluid, the flux of energy due to deformation is

$$I_{E,comp} = -P\dot{V} \tag{10.58}$$

where P is the total pressure of the fluid. Again, we will follow the derivation introduced above, which leads to

$$\dot{E} + P\dot{V} - I_{E,th} - T\left[\dot{S} - I_S - \Pi_S\right] - \sum_{i=1}^{N} \mu_i\left[\dot{n}_i - \Pi_{ni}\right] = 0 \tag{10.59}$$

as a consequence of the fact that all equations of balance should be satisfied simultaneously. To simplify the work, we have assumed the Lagrange multipliers to be known. This equation is easily rearranged as follows:

$$\underbrace{\dot{E} + P\dot{V} - T\dot{S} - \sum_{i=1}^{N} \mu_i\dot{n}_i}_{=0} - \underbrace{I_{E,th} + T I_S}_{=0} + \underbrace{T\,\Pi_S + \sum_{i=1}^{N} \mu_i\Pi_{ni}}_{=0} = 0 \tag{10.60}$$

For the same reasons as given above, the first and the second terms must be equal to zero, which leads to the main result of the present case:

$$\dot{E} + P\dot{V} - T\dot{S} - \sum_{i=1}^{N} \mu_i\dot{n}_i = 0 \tag{10.61}$$

$$T\,\Pi_S + \sum_{i=1}^{N} \mu_i\Pi_{ni} = 0 \tag{10.62}$$

The first of these expressions is the Gibbs fundamental form of a fluid composed of different substances, while the second demonstrates how much entropy is produced as a consequence of the irreversible reactions between species.

Consequences of the theory are derived in a manner very similar to what we have seen in Section 10.2. We have taken the energy and the entropy of the fluid to be functions of volume, temperature, and N species. If we perform partial derivatives on the Gibbs fundamental form, Equ.(10.61), and collect the terms, we get

$$\left[\frac{\partial E}{\partial V}-T\,\frac{\partial S}{\partial V}+P\right]\dot{V}+\left[\frac{\partial E}{\partial T}-T\,\frac{\partial S}{\partial T}\right]\dot{T}+\sum_{i=1}^{N}\left[\frac{\partial E}{\partial n_i}-T\,\frac{\partial S}{\partial n_i}-\mu_i\right]\dot{n}_i=0$$

Since every one of the independent variables can be changed independently of the others, each of the terms in brackets must be zero:

$$\begin{aligned}\frac{\partial E\left(V,T,n_1\ldots n_N\right)}{\partial V}&=T\,\frac{\partial S\left(V,T,n_1\ldots n_N\right)}{\partial V}-P\left(V,T,n_1\ldots n_N\right)\\ \frac{\partial E\left(V,T,n_1\ldots n_N\right)}{\partial T}&=T\,\frac{\partial S\left(V,T,n_1\ldots n_N\right)}{\partial T}\end{aligned} \qquad \textbf{(10.63)}$$

and

$$\frac{\partial E\left(V,T,n_1\ldots n_N\right)}{\partial n_i}=T\,\frac{\partial S\left(V,T,n_1\ldots n_N\right)}{\partial n_i}+\mu_i\left(V,T,n_1\ldots n_N\right) \qquad \textbf{(10.64)}$$

for $i = 1\ldots N$. These relations are similar, but not equal, to what we have derived in Equ.(10.42). In that case, the relations held for each individual phase composed of only one species. In our current case, on the other hand, E and S are the energy and the entropy of the entire mixture, and we have a total of N equations of the form given in Equ.(10.64), where the derivatives of these functions are taken with respect to each of the species of the mixture.

EXERCISES AND PROBLEMS

1. Consider a uniform viscous fluid like the one introduced in Section 10.1. Let the fluid have a pressure, and entropy capacitance, and a latent entropy like the ideal gas, but let friction be present. (a) Show that the energy added in heating of the fluid at constant volume is

$$E_{th}=E\left(V,T_f\right)-E\left(V,T_i\right)$$

where the indices i and f refer to the initial and the final states, respectively. (b) Consider heating at constant pressure. Show that, in this case, the energy added in heating can be expressed as

$$E_{th}=H\left(P,T_f\right)-H\left(P,T_i\right)+\int_{t_i}^{t_f} a\dot{V}^2 dt$$

Show that this quantity is always less than the difference of the enthalpies at the end and the beginning. (c) Assume the friction factor a, the rate of change of the volume, and the energy current in heating to be given. Assume the rate of change of the volume to be constant. Show that the initial value problem of the fluid takes the form

$$\begin{aligned}&\frac{C_V}{T}\dot{T}-\frac{1}{T}I_{E,th}(t)+\frac{a}{T}\dot{V}^2=-\frac{nR}{V_0+\dot{V}\,t}\dot{V}\\ &T(t=0)=T_0\end{aligned}$$

where V_0 is the volume at $t = 0$.

2. Consider the uniform viscous fluid described in Problem 1. Show that for isothermal heating at a temperature T with prescribed entropy current $I_S(t)$, the differential equation for the volume becomes

$$\frac{a}{T}\dot{V}^2 + \frac{nR}{V}\dot{V} = I_S(t)$$

3. Derive the initial value problem for adiabatic processes of an ideal gas having internal friction according to the model of Section 10.1. Assume the rate of change of volume to be given as a particular function of time.
4. (a) Show how to obtain the temperature and the pressure of a simple fluid as derivatives of the energy function. (b) Derive the energy of the ideal gas as a function of S and V. Show that you can obtain both the entropy as a function of temperature and volume, and the equation of state of the ideal gas from this information.
5. Isothermal and adiabatic compressibilities, κ_T and κ_S, are defines as follows:

$$\kappa_T = -\frac{1}{V}\frac{\partial V(P,T)}{\partial P} \quad , \quad \kappa_S = -\frac{1}{V}\frac{\partial V(P,S)}{\partial P}$$

Demonstrate that κ_T and κ_S, are related by the factor γ (the ratio of the specific heats).

6. For the uniform fluids treated in Section 10.1, show that

$$\Lambda_V = \frac{\partial P(V,T)}{\partial T}$$

7. The thermal coefficient of expansion is defined as $\alpha_V = (1/V)\partial V(P,T)/\partial T$. Prove the following relationship:

$$K_P - K_V = V\frac{\alpha^2}{\kappa_T}$$

Transform this relation to show that the specific temperature coefficients of enthalpy and of energy are related by

$$c_P = c_V\left(1+\gamma^*\alpha_V T\right) \quad , \quad \gamma^* = \frac{\alpha_V}{\rho c_V \kappa_T} = \frac{\alpha_V}{\rho c_P \kappa_S}$$

where γ^* is called the Grüneisen ratio. (κ_S is the adiabatic compressibility, respectively.) Show that the Grüneisen ratio for the ideal gas is

$$\gamma^* = \frac{c_P}{c_V} - 1 = \gamma - 1$$

8. Assume that the density $\rho(T)$, the specific entropy capacitance $\kappa_P(T)$ at constant pressure, and the speed of sound c in a fluid are known from experiments as functions of temperature for a given pressure. Determine from these values the ratio of the specific heats γ, the (isothermal) compressibility κ_T, and the latent entropy with respect to volume.
9. Show that the law of adiabatic change of an ideal fluid written with temperature and density as the independent variables is given by

$$\left.\frac{dT}{d\rho}\right|_{ad} = \frac{T}{\rho}\gamma^*$$

where γ^* is the Grüneisen ratio defined in Problem 7.

CHAPTER 11

THERMODYNAMICS OF CONTINUOUS SYSTEMS

So far we have used laws of balance and expressions for processes, i.e., for flows, source rates and production rates, in their integral forms; in other words we have written and applied the appropriate equations for an entire body. Now we will justify and derive the proper equations of balance of mass, entropy, and momentum, for continuous bodies. This will prepare the ground for theories of thermodynamics of continuous processes which build upon these laws of balance and expressions for constitutive laws in analogy to how we have proceeded before in this book.

I would like to emphasize that the following development will not be rigorous in either the mathematical or the physical senses. Mathematical derivations will be performed for the simplest geometrical cases of purely one-dimensional transports only, and the physical scope of the laws will be limited to relatively simple phenomena.[1] Still, I will use ideas in their most fundamental form to motivate the laws of balance and some simple constitutive relations of continuum physics, and general results will be presented as extensions of simpler ones. The result will be an uncluttered presentation of a subject often deemed difficult for beginners.

11.1 LIFE AND MIGRATION OF LOCUSTS

Let me introduce the ideas and some simple mathematical forms of spatially continuous processes by discussing a particularly vivid case, namely, the migration of locusts. As mentioned above, I will make many simplifying assumptions, but this will not limit the importance of the results. The discussion will be exactly what we need as begin-

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[1] Neither restriction will fundamentally limit the applicability of the ideas. The general mathematical forms for more complicated three-dimensional flow processes have the same basic appearance as the simple one-dimensional ones. We will simply suggest that the derivations presented here will carry over to the more advanced cases. When terms representing particular physical phenomena are left out of an equation for simplicity, it is assumed that they could be included similarly to other terms for which the derivation is presented. Those of you who wish to see a more rigorous treatment of the subject should turn to books on fluid dynamics and continuum mechanics. See, for example, Malvern, 1969; Mase, 1970; Landau and Lifshitz, 1959; Lai, Rubin, and Krempl, 1978; and Whitaker, 1968.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_12,

ners if we want to connect understanding to formalism.

First of all, assume that the space in which locusts live is a very thin strip on the ground effectively creating a single-dimensional domain (Fig. 11.1). The area (inside) of the strip will be called *volume* even though it is not three-dimensional, and the sides of the domain will be called *surface*. At any given moment, there are certain numbers of insects in different parts (elements) of their domain, and these numbers change from place to place and in the course of time. Let us assume that there are always so many insects that we cannot make out an individual one. Rather, we will see them as a continuous mass distributed in space.

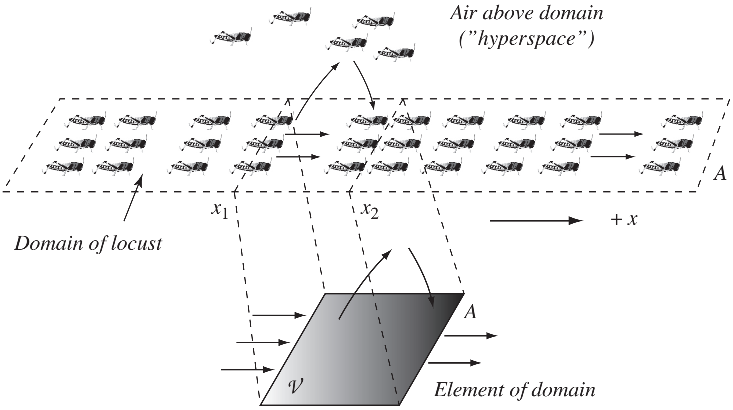

Figure 11.1: locusts in a single-dimensional domain (in the strip, there is never any variation perpendicular to the x-direction). The insects can move in the x-direction (positive or negative), and they can jump into or out of "hyperspace." A part of the domain (element) has been singled out for formulating the law of balance of locusts. The shades of gray indicate locust density, the arrows symbolize processes. A is the width of the domain perpendicular to x, and x_1 and x_2 denote the ends of the element chosen for analysis.

When the insects fly, they are no longer part of their space. We can imagine the air above the strip on which they live to be a "hyperspace" that allows the insects to disappear at a point and reappear at some other point without moving through the domain itself; this is a vivid description of radiative processes. In the domain itself, the insects can crawl in either direction, and they can be swept along with water if there is a stream in (parts of) their space. These processes are analogs of what we call conduction and convection in physics. Apart from these transport processes, the insects can be born and die. All the processes taken together are responsible for changing the numbers of insects in their space which leads to the law of balance for locusts.

There will be particular circumstances that determine the processes. Such circumstances are the numbers of insects at different locations, food resources, water on the ground, currents of air, etc. We can even imagine more complex phenomena where processes influence other processes or feed back on themselves, and just possibly the history of the system might have an impact upon what is going on later. Such circumstances are the basis of what we call constitutive laws.

11.1.1 Locust Density and Densities of Process Quantities

In a description of spatially continuous systems, the number of locusts and quantities denoting processes such as currents and production rates vary from point to point in the domain in which the insects live. At any given time, the quantities we use to describe the system are functions of position.

Density of locusts. Take the number of locusts at a point of the domain, i.e., at some location x. We want to assume that there is absolutely no variation perpendicular to the direction of x. Apparently, defining the number of insects at a point does not make much sense. Rather, we need to know the density of locusts as a measure of their distribution in space. From this density, the number of insects in the entire domain or a part thereof, i.e., in an element (Fig. 11.1), can be calculated. Assume the element to be fixed in space and call $\rho_L(x,t)$ the density of locusts which is a function of position and time. Then

$$n_L(t) = \int_{\mathcal{V}} \rho_L(x,t)\,dV = \int_{x_1}^{x_2} \rho_L(x,t)\,A\,dx \tag{11.1}$$

is the number of insects in the element shown in Fig. 11.1. A is the surface (side) of this element which extends from x_1 to x_2; $\mathcal{V}$ is the two-dimensional volume of the element. Remember that the density of insects does not vary except in then x-direction.

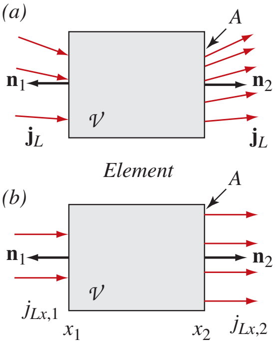

Figure 11.2: Distribution of currents on the surface of an element. (a) General case, (b) purely single dimensional transport. If the dot product of the current density vector and the surface normal vector of unit length are calculated, the component (including sign) of the current density is obtained.

Conductive transports. Now turn to insects crawling in their space, i.e., either in positive or in negative x-direction; we will deal with the other processes a little later. As far as our element is concerned, the insects crawl across its surfaces at x_1 and x_2 (see Fig. 11.2). The transports are described as conductive currents. Since the number of locusts crossing a boundary per unit of time can vary on that boundary—here, perpendicularly to the x-direction—the transport process is described by a *current density* $\mathbf{j}_L$ on the line of width A. Since the insects could crawl in any direction on the ground at the location of the boundary, a current density is a vector quantity. Naturally, we shall continue to assume that they move only in x-direction (positive or negative), and that the current density does not vary except in x-direction (Fig. 11.2, b). This will make the mathematics very simple: we only have an x-component j_{Lx} of the vector. The net current of locusts is determined as the integral of the current density over the total surface $\mathcal{A}$ of the element:

$$I_{L,i}(t) = -\int_{\mathcal{A}} \mathbf{j}_L \cdot \mathbf{n}_i(x_i,t)\,dA \tag{11.2}$$

The component of $\mathbf{j}_L$ used to calculate the current is obtained by the dot product with the surface normal vector $\mathbf{n}_i$ at location x_i (Fig. 11.2).[2] In our strongly simplified case, the current turns out to be equal to $j_{Lx}A$ at x_1 and equal to $-j_{Lx}A$ at x_2. This still allows the insects to crawl in either positive or negative direction at the two surfaces of the element in Fig. 11.1; the direction is defined by the sign of j. The net conductive current is therefore

$$I_{L,net}(t) = -\left(j_{L,2}(t) - j_{L,1}(t)\right)A \tag{11.3}$$

Births and deaths. For now, take a look at how to describe births and deaths, i.e., the processes of production and destruction of the species—very much like a chemical reaction (Chapter 6). What is the production rate of locusts $\Pi_L(t)$ in the element with

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[2] In mathematics, it is standard practice to choose the outward direction of a surface of a system as the positive direction. This means that the surface normal vector points outwards (see Fig. 11.2). Since we count a current going into a system as a positive quantity, this leads to the negative sign in Equ.(11.2).

volume $\mathcal{V}$? Since the process can vary spatially *inside* the system, it has to be described by a volume density—a quantity distributed in space. The resulting quantity for the element is the integral of the *production rate density* π_L over the volume:

$$\Pi_L(t) = \int_{\mathcal{V}} \pi_L(x,t)\,dV = \int_{x_1}^{x_2} \pi_L(x,t) A\,dx \tag{11.4}$$

As for everything else in this example, we assume that the production rate density varies only in x-direction.

11.1.2 A Law of Balance of Locusts

Now we are prepared to formulate a first version of a law of balance for the element under consideration. The number of locusts in the element changes because of migration on the ground (conduction) and births and deaths (production). The law of balance of locusts is therefore

$$\frac{d}{dt} n_L(t) = I_{L,net}(t) + \Pi_L(t) \tag{11.5}$$

n_L, I_L, and Π_L are given by Equations (11.1), (11.3), and (11.4). Two of these are volume integrals, the second—the expression for the net current—looks different. Interestingly, it can be transformed into a volume integral as well. For the simple case discussed here, the formalism can be described quite intuitively. The net current equals the difference of the current densities at the ends of the element. This difference can be obtained as the integral in the x-direction of the (spatial rate of) change of $j_x(x)$:

$$I_{L,net}(t) = -\big(j_L(x_2,t) - j_L(x_1,t)\big)A = -\int_{x_1}^{x_2} \frac{\partial j_{Lx}(x,t)}{\partial x} A\,dx$$

or

$$I_{L,net}(t) = -\int_{\mathcal{V}} \frac{\partial j_{Lx}(x,t)}{\partial x} dV \tag{11.6}$$

Now the pieces can be assembled and combined. Inserting Equations (11.1), (11.4), and (11.6) into (11.5) leads to

$$\frac{d}{dt}\int_{\mathcal{V}} \rho_L(x,t)\,dV = -\int_{\mathcal{V}} \frac{\partial j_{Lx}(x,t)}{\partial x} dV + \int_{\mathcal{V}} \pi_L(x,t)\,dV$$

Since the element is fixed in space, the time derivative of the integral on the left can be transformed into

$$\frac{d}{dt}\int_{\mathcal{V}} \rho_L(x,t)\,dV = \int_{\mathcal{V}} \frac{\partial \rho_L(x,t)}{\partial t} dV$$

Now we have

$$\int_{\mathcal{V}} \frac{\partial \rho_L(x,t)}{\partial t} dV + \int_{\mathcal{V}} \frac{\partial j_{Lx}(x,t)}{\partial x} dV - \int_{\mathcal{V}} \pi_L(x,t)\,dV = 0$$

or

$$\int_{\mathcal{V}}\left[\frac{\partial\rho_L(x,t)}{\partial t}+\frac{\partial j_{Lx}(x,t)}{\partial x}-\pi_L(x,t)\right]dV=0$$

There is one final step to be made which is based upon an interpretation of the last expression. The combined terms in brackets can basically take any values, meaning that their integral over the fixed volume of the element should not generally equal zero. However, since the integral does vanish, the term in brackets must be equal to zero for all values of x and t, so

$$\frac{\partial\rho_L(x,t)}{\partial t}+\frac{\partial j_{Lx}(x,t)}{\partial x}=\pi_L(x,t) \tag{11.7}$$

This is called the *local* or *differential form of the law of balance* (of locusts) in contrast to the integral form in Equ.(11.5). Since there are derivatives with respect to time and position, the equation is a partial differential equation for the density, production rate density, and current density. It still looks similar to the integral law of balance and, with a little bit of practice, can be read, written, and understood almost as easily as the simpler forms we have been using so far. We just have to get used to thinking in terms of densities and remember that the local change of the current density[3] matters—not the current density itself.

11.1.3 Some Simple Constitutive Relations

If the laws of balance are the trunk of a tree, constitutive relations are its branches. The image tells us something about the possible complexity of special material laws. I do not intend to create a biologically viable theory here, so I will present just a couple of the simplest possible relations that let us put branches onto Equ.(11.7).

Dying of locusts. Assume that in the time span of interest to us, locusts are not born; they only die. One of the simplest ideas for a model of a death rate is to set it proportional to the instantaneous number of insects living in a system. Therefore, the production rate density must be proportional to the density of the insects:

$$\pi_L(x,t)=-f_D\rho_L(x,t) \tag{11.8}$$

f_D is a factor describing the speed at which a population would die out according to this relation—it is similar to a decay constant in radioactive decay.

Crawling of insects. Another simple idea used in biology that looks similar to examples found in physics and chemistry, deals with the migration of animals. Assume that locusts tend to migrate in their space in the direction of lower insect density. Describing this idea with formal tools is quite simple (Fig. 11.3). Imagine the density as a function of position to form a kind of landscape with the density as the level. Where the landscape is steeper, the flow will be stronger. The quantity measuring how steep

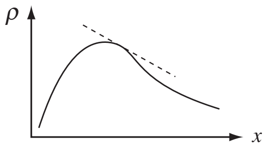

Figure 11.3: The density of locusts as a function of position creates a kind of landscape. The slope of this landscape determines the strength of a diffusive flow.

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[3] The partial derivative of the single component of the current density is the single-dimensional form of what is called the divergence of the current density vector (see Section 11.2.5).

the density landscape is, is called the *gradient* of the density, $\partial \rho_L / \partial x$. So, the conductive current density of locusts may be set proportional to this gradient:

$$j_{Lx}(x,t) = -k \frac{\partial \rho_L(x,t)}{\partial x} \tag{11.9}$$

The factor k is Equ.(11.7) a kind of conductivity or diffusion coefficient. The minus sign tells us that the flow is in the direction of decreasing density. Even though the gradient looks just like the divergence (Equ.(11.7)) in a single spatial dimension, gradient and divergence are two very different mathematical quantities.

The field equation for density. If the particular relations for the production rate density and the current density are introduced into the equation of balance, Equ.(11.7), we obtain a partial differential equation for the density:

$$\frac{\partial \rho_L(x,t)}{\partial t} + \frac{\partial}{\partial x}\left(-k \frac{\partial \rho_L(x,t)}{\partial x}\right) = -f_D \rho_L(x,t) \tag{11.10}$$

In continuum physics, an equation of this type is called a *field equation*. There are two types of side conditions that have to be specified for a concrete solution: we need an *initial condition* and *boundary conditions*. The initial condition might specify the density in the entire domain at an initial point of time. In the simple case discussed here, there will be boundary conditions at either end of the domain, i.e., at $x = 0$ and $x = L$. The conditions can take different forms. For example, the density may be prescribed at either end of the space, or the flows may be given, or we may have a mixture of these forms. Depending upon all the details, the differential equation and its side conditions need to be solved numerically.

11.1.4 Radiation and Convection

To finish this introductory example, let me briefly describe how we can deal with the other two types of processes: radiation and convection of locusts. The former will be identified with flying locusts, the latter may be thought of as occurring if the insects are swept along with a stream of water.

Radiative process. When the insects fly off, they leave their domain at the spot where they were and lift off into what I called "hyperspace." When they land again, they appear in the domain at a point. The process looks clearly like what we know from radiation (see Chapters 7 and 12). Radiation is described by source rates. All we have to do to apply the idea to the continuous case is to introduce a *source rate density* σ. The source rate of locusts in an element (as in Fig. 11.1) is determined as the volume integral of the source rate density:

$$\Sigma_L(t) = \int_{\mathcal{V}} \sigma_L(x,t)\, dV \tag{11.11}$$

This is equivalent to the relation between production rate and production rate density defined in Equ.(11.4). Indeed, from a mathematical point of view, there is no difference between production and radiation for the system under consideration. The difference lies in the fact that, in the case of radiation, the insects come from a different space—they are not born, i.e., not created out of nothing.

Convective transport. As we have seen in Chapter 8, convective transports are described by currents. This means that the mathematical forms used for conductive currents apply as well: there is a current density (a function distributed over the surface of an element) and the divergence of this current density appears in the law of balance.

The only difference is in the particular form of the current. Imagine the locusts to be caught by a stream, and their density in the water is ρ_L. We can directly apply the ideas developed in Section 8.2.1 (see Fig. 8.3 and Equ.(8.3)). In the purely one-dimensional case, the convective current of insects turns out to be equal to $I_{L,conv} = A\rho_L v$, where v is the flow speed of the water. The *convective current density* $j_{L,conv}$ of locusts must then equal

$$j_{L,conv} = \rho_L v \tag{11.12}$$

This form introduces a new quantity, namely, the flow speed that must be obtained from some other information. In continuum physics, flow speed would be the solution of a continuum model of the fluid. This means that a model involving convective processes is generally a coupled problem dealing with the species in question and the fluids that lead to convection.

General form of the law of balance of locusts. We can now combine the expressions for the additional processes with the law of balance of locusts. The integral form of the law of balance is

$$\frac{d}{dt} n_L(t) = I_{L,cond,net}(t) + I_{L,conv,net}(t) + \Sigma_L(t) + \Pi_L(t) \tag{11.13}$$

If we apply the same reasoning that led to Equ.(11.7), we obtain

$$\frac{\partial \rho_L}{\partial t} + \frac{\partial}{\partial x}\left(j_{Lx,cond} + \rho_L v\right) = \sigma_L + \pi_L \tag{11.14}$$

for the most general local form of the law of balance of locusts. Again, with a little practice, one can understand such equations quite easily.

In the following sections, we are going to study a generalized version of the case of locusts, but applied to the phenomena of physics we are accustomed to. First, the terms needed for a continuum description will be introduced, then the laws of balance of mass, momentum, and entropy will be formulated before we finally turn to an example of a continuum theory of thermodynamics. Such a theory involves constitutive laws in addition to the laws of balance.

11.2 DENSITIES AND CURRENT DENSITIES

Equations of balance for a body relate the rate of change of system content, currents across the surface of the system, and possibly, source rates and rates of production. They tell us how quantities such as mass, entropy, and momentum of a body change as a result of flow processes, and where appropriate, as a consequence of absorption and production. While in integral form, these quantities refer to an entire body, in continuous processes they have to be transformed to reflect their distribution in space. Entering these distributions into the well-known forms of the equations of balance will yield the desired result, namely equations of balance for continuous processes.

11.2.1 The Density of Fluidlike Quantities

Figure 11.4: The density of a quantity tells us about its distribution over a volume. Where the density is higher, more "stuff" is contained in a part of space. If the density changes in space, we have to integrate the distribution over volume to obtain the amount of the quantity contained in a system.

We have come across an example of a density in our discussion of locusts. The density of a fluidlike quantity is our means of telling how the quantity is distributed over a given volume. The concept is easily grasped: if it is constant, the density multiplied by the volume tells us how much of the quantity is contained in the volume; if it is variable, we simply have to integrate the density over the volume to obtain the desired result (Fig. 11.4). A density is commonly introduced for the mass of a body. Integrating the mass density ρ_m over volume yields the mass of the body contained in the volume:

$$m = \int_{\mathcal{V}} \rho_m \, dV \tag{11.15}$$

This carries over to all quantities of a similar type, including entropy, momentum, and energy. If we write ρ_Q for the density of a particular quantity, the amount Q of this quantity contained in a given volume is calculated according to

$$Q = \int_{\mathcal{V}} \rho_Q \, dV \tag{11.16}$$

For our current purpose, this definition is applied to entropy, mass, and momentum of a system. It has been presented for mass in Equ.(11.15); as is customary in this special case, we will not use the subscript m to denote mass: the symbol ρ is used for the mass density of a body. The density of a particular quantity is often written in terms of the *specific* value $q = Q/m$ of the quantity and the mass density of the material containing the quantity:

$$\rho_Q = \rho q \tag{11.17}$$

Using this form, Equ.(11.16) becomes

$$Q = \int_{\mathcal{V}} \rho q dV \tag{11.18}$$

Entropy. Entropy is the fluidlike quantity of thermal processes. If we apply the general expressions formulated above, we obtain the following equations for the entropy of a system:

$$S = \int_{\mathcal{V}} \rho_S \, dV = \int_{\mathcal{V}} \rho s dV \tag{11.19}$$

Momentum. For momentum, we obtain a perfectly analogous equation, at least in the one-dimensional case:

$$p = \int_{\mathcal{V}} \rho_p \, dV = \int_{\mathcal{V}} \rho v dV \tag{11.20}$$

The velocity v of matter represents its specific momentum, i.e., its momentum per mass. Since momentum is a vector, we either have to write Equ.(11.20) as one vector equation or as three component equations (in a Cartesian coordinate system):

$$\mathbf{p} = \int_{\mathcal{V}} \rho \mathbf{v} \, dV \tag{11.21}$$

or

$$\begin{aligned} p_x &= \int_{\mathcal{V}} \rho v_x \, dV \\ p_y &= \int_{\mathcal{V}} \rho v_y \, dV \\ p_z &= \int_{\mathcal{V}} \rho v_z \, dV \end{aligned} \tag{11.22}$$

If we work with the components of momentum in a Cartesian coordinate system,[4] we can deal with definitions and laws as if momentum consisted of three independent scalar quantities with properties similar to those of mass or entropy.

11.2.2 Source Rate Densities and Production Rate Densities

Some of the fluidlike quantities change as a consequence of source or production processes. Sources are used to describe the interaction of bodies and fields where quantities are transported into and out of bodies without crossing their surfaces. Quantities transferred in this way either originate or end up in another system; they are not produced in this manner. Since a source rate tells us the rate at which a fluidlike quantity appears or disappears inside a body, and since this rate may be different in different parts of a body, we again introduce the concept of a distribution function, this time of the source rate over a volume. In other words, we use the spatial density σ_Q of the source rate Σ_Q to quantify its distribution. The relation between the source rate and its density is known from the density of a quantity:

$$\Sigma_Q = \int_{\mathcal{V}} \sigma_Q \, dV = \int_{\mathcal{V}} \rho f_Q \, dV \tag{11.23}$$

where f_Q is the specific source rate (source rate per mass). If you wish to use this expression for a particular physical quantity such as entropy or momentum,[5] you have to substitute that quantity for Q. Remember, in the case of momentum you have to write three independent equations for each of the Cartesian components of the momentum vector.

The same idea applies to the phenomenon of the production of a quantity. Again, the rate of production may vary over the volume of a system, in which case we should introduce the spatial density π_Q of the rate of production Π_Q:

$$\Pi_Q = \int_{\mathcal{V}} \pi_Q \, dV \tag{11.24}$$

Of the quantities we are dealing with in this chapter—mass, entropy, momentum, and energy—only entropy admits a (strictly non-negative) production term.

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[4] For reasons of simplicity, whenever multidimensional forms of equations of balance will be written in component form, a rectangular Cartesian coordinate system will be chosen. More general coordinate systems are treated in books on continuum mechanics (for example, Malvern, 1969).

[5] As you know, there is no source term of mass if we use mass as a measure of amount of substance (as we currently do). Substances cannot be transferred radiatively. If we actually had to deal with mass as in gravitational processes, the equivalence of mass and energy tells us that there could be radiative sources of mass in a system.

11.2.3 Current Densities

The current density (or flux density) of a fluidlike quantity is used as the measure of the distribution of a current over a surface, just as the density is used to describe the distribution of a fluidlike quantity in space (see Fig. 11.5).

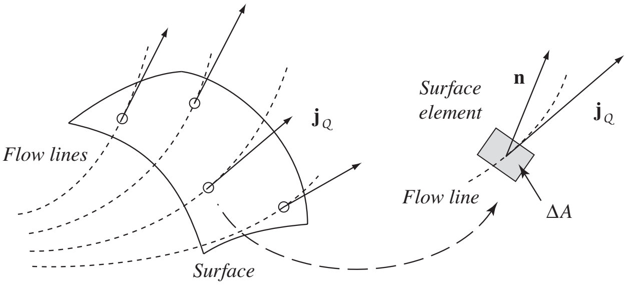

Figure 11.5: Flow lines cutting through a surface present an image of the distribution of a current. The distribution is measured in terms of the current density over the surface. Note that the flux density of a scalar quantity is a vector with a direction tangential to the flow line. The orientation of this vector with respect to the surface normal vector **n** is used when calculating the flux of the quantity transported through space.

Let us start with the simplest possible case of a current density and its associated current or flux, namely that of a flow perpendicular to a flat surface having a constant value of the current density on the surface. Naturally, in this case the flux is calculated simply as the product of the absolute value of the current density and the surface area. With a given orientation of the surface, the value of the flux is taken to be *negative* if the current flows in the direction of the normal vector representing the orientation. This means that, in this simple case, we can write the flux in the following form:

$$I_Q = -A\,\mathbf{j}_Q \cdot \mathbf{n} \tag{11.25}$$

The dot denotes the scalar product of the vectors $\mathbf{j}_Q$ and $\mathbf{n}$. As before, for a surface of a body, we will take the orientation positive for outward direction (Fig. 11.6). We can now relax the condition that the flow must be perpendicular to the flat surface. The same form as in Equ.(11.25) still applies; and it does so as well for a small part of a curved surface cut by arbitrary flow lines as depicted in Fig. 11.5. In general, then, the flux of an arbitrary flow field cutting through a curved surface must be given by the surface integral

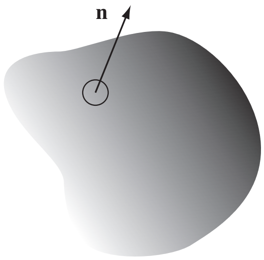

Figure 11.6: The orientation of the surface of a body is taken to be positive for the outward direction. The normal vector **n** points away from the body.

$$I_Q = -\int_{\mathcal{A}} \mathbf{j}_Q \cdot \mathbf{n}\, dA \tag{11.26}$$

where $\mathcal{A}$ is the surface under consideration. This surface may be the closed surface of a body or a part thereof.

Remember that we have to distinguish between two different types of currents if we are dealing with material systems,[6] namely those associated with convective and conductive transports. If a fluidlike quantity flows through matter, the flux is said to be conductive; if it flows with matter, we call the transport convective. Conductive transports are quantified in terms of a conductive current density $\mathbf{j}_Q^{(c)}$. The convective cur-

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[6] There is a third type of current or flux associated with the transport of a fluidlike quantity through a field.

rent, on the other hand, can be expressed in terms of the specific value of the quantity transported by matter and the flux of mass; see Section 8.2 of Chapter 8:

$$I_{Q,conv} = qI_m \tag{11.27}$$

All we must do to obtain the continuum form of this relation is to calculate the flux of mass for the spatially variable case. You know that the flux of mass is equal to the product of the density of the material and its flux of volume. The latter quantity must be given by the integral of the volume flux density over the surface:

$$I_V = -\int_{\mathcal{A}} \mathbf{j}_V \cdot \mathbf{n}dA = -\int_{\mathcal{A}} \mathbf{v} \cdot \mathbf{n}dA \tag{11.28}$$

As you can see, the volume flux density is equal to the speed of flow:

$$\mathbf{j}_V = \mathbf{v} \tag{11.29}$$

Therefore, the flux density of mass is the product of the density and the speed of flow:

$$\mathbf{j}_m = \rho\mathbf{v} \tag{11.30}$$

This tells us that the convective current density of a quantity Q is given by the product of the specific quantity and the mass flux density:

$$\mathbf{j}_{Q,conv} = q\rho\mathbf{v} \tag{11.31}$$

Now, we have the means of expressing the total flux density of a particular quantity, namely by adding up the conductive and the convective parts:

$$\mathbf{j}_Q = q\rho\mathbf{v} + \mathbf{j}_Q^{(c)} \tag{11.32}$$

and, for stationary control volumes, the flux turns out to be

$$I_Q = -\int_{\mathcal{A}} \left(q\rho\mathbf{v} + \mathbf{j}_Q^{(c)} \right) \cdot \mathbf{n}dA \tag{11.33}$$

11.2.4 Current Densities of Mass, Entropy, and Momentum

To obtain the expressions pertaining to the particular quantities with which we are dealing, we simply have to replace the general quantity Q by either mass, entropy, or momentum. Since mass (amount of substance) does not have a conductive flux, the total flux density is given by the expression in Equ.(11.30):

$$\mathbf{j}_m = \rho\mathbf{v} \tag{11.34}$$

Entropy is a fairly simple case since this quantity is a scalar just like mass or electric charge. The specific entropy is abbreviated by s, while the conductive current density of entropy is written as $\mathbf{j}_S^{(c)}$:

$$\mathbf{j}_S = s\rho\mathbf{v} + \mathbf{j}_S^{(c)} \tag{11.35}$$

Momentum, on the other hand, presents us with a more complicated case since we have to deal with a vectorial quantity. The problem is simplified if we treat each of the components of the vector independently. As you recall from the brief presentation in Chapter 3, a component of momentum can be thought of as flowing through matter much like entropy or charge do. The flow of each of the components of momentum results in a flow field like those shown in Chapter 3 and below in Fig. 11.7.

Here are the equations for a single component of momentum. You can build the complete result for all three components by combining the parts. If we choose the *x*-component, the specific value of *x*-momentum p_x is the *x*-component of the velocity. Therefore, we have

$$\mathbf{j}_{px} = \rho v_x \mathbf{v} + \mathbf{j}_{px}^{(c)} \tag{11.36}$$

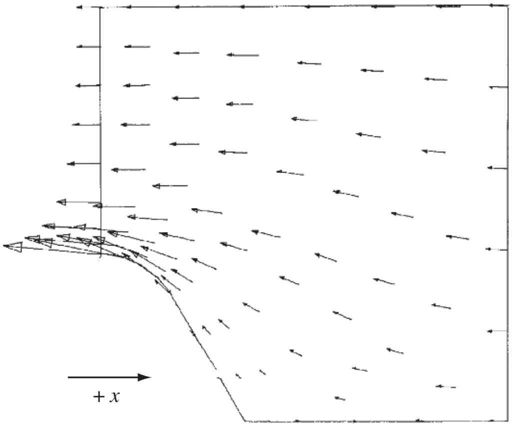

Figure 11.7: Flow pattern of one component of momentum resulting from tension in a flat strip having a notch. The component of momentum whose flow is depicted here is the one identified with the direction of tension. See also Fig. 3.8.

In this case it might be instructive to present all three components of the current density:

$$\begin{aligned} j_{pxx} &= \rho v_x v_x + j_{pxx}^{(c)} \\ j_{pxy} &= \rho v_x v_y + j_{pxy}^{(c)} \\ j_{pxz} &= \rho v_x v_z + j_{pxz}^{(c)} \end{aligned} \tag{11.37}$$

These quantities have a simple graphical representation; j_{pxx}, for example, represents the current density of *x*-momentum flowing in *x*-direction, while j_{pxy} is the current density of *x*-momentum flowing in *y*-direction (see Fig. 11.7) Since there are three components of current density vectors belonging to the three components of momentum, a total of nine components[7] form the momentum current density tensor.

11.2.5 Transformation of a Surface Integral (Divergence Theorem)

In Section 11.1.2, we transformed a surface integral into an integral over the volume bounded by the surface. We treated the simple example of purely one-dimensional migration of locusts. Since the number of locusts is a scalar quantity, its current density is a vector describing the three possible directions of flow of this fluidlike quantity. If the current density vector has only one component, then locusts move in only one direction. In this case, the locusts flux is

$$I_{Lx} = -\int_{\mathcal{A}} \mathbf{j}_L \cdot \mathbf{n}_x \, dA \overset{def}{=} -\int_{\mathcal{A}} j_{Lx} \, dA$$

The second form on the right has been introduced to shorten the notation. This integral can be transformed into a volume integral according to

$$I_L = -\int_{\mathcal{A}} j_{Lx} \, dA = -\int_{\mathcal{V}} \frac{\partial}{\partial x} j_{Lx} \, dV$$

We used this relation to derive the local form of the equation of balance of locusts above in Section 11.1.2 (see Equ.(11.6)). In this form, the transformation is the simplest example of what is called the *divergence theorem* or *Gauss's theorem*. Let me briefly write down this relation without giving a proof.[8] If we define a current density vector $\mathbf{j}_Q$ on the closed surface of a body, the surface integral can be transformed into an integral over the volume enclosed by the surface:

$$\int_{\mathcal{A}} \mathbf{j}_Q \cdot \mathbf{n} dA = \int_{\mathcal{V}} \nabla \cdot \mathbf{j}_Q dV \tag{11.38}$$

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7. This quantity cannot be represented as a vector anymore; rather, it is a tensor which may be written in matrix form

$$\mathcal{J}_p = \begin{pmatrix} \rho v_x v_x + j_{pxx}^{(c)} & \rho v_x v_y + j_{pxy}^{(c)} & \rho v_x v_z + j_{pxz}^{(c)} \\ \rho v_y v_x + j_{pyx}^{(c)} & \rho v_y v_y + j_{pyy}^{(c)} & \rho v_y v_z + j_{pyz}^{(c)} \\ \rho v_z v_x + j_{pzx}^{(c)} & \rho v_z v_y + j_{pzy}^{(c)} & \rho v_z v_z + j_{pzz}^{(c)} \end{pmatrix}$$

The negative conductive part of this quantity is commonly called the *stress tensor*

$$\mathcal{T} = \begin{pmatrix} t_{xx} & t_{xy} & t_{xz} \\ t_{yx} & t_{yy} & t_{yz} \\ t_{zx} & t_{zy} & t_{zz} \end{pmatrix} = -\begin{pmatrix} j_{pxx}^{(c)} & j_{pxy}^{(c)} & j_{pxz}^{(c)} \\ j_{pyx}^{(c)} & j_{pyy}^{(c)} & j_{pyz}^{(c)} \\ j_{pzx}^{(c)} & j_{pzy}^{(c)} & j_{pzz}^{(c)} \end{pmatrix}$$

while the complete quantity would be called the *momentum current tensor.* The surface integral of a row of the tensor (for one of the components of the coordinate systems) is called the component of the surface force

$$F_x = \int_{\mathcal{A}} \mathbf{T}_x \cdot \mathbf{n} dA$$

($\mathbf{T}_x$ is the first row of the stress tensor), while the surface integral for the stress tensor is the surface force vector

$$\mathbf{F} = \int_{\mathcal{A}} \mathcal{T} \cdot \mathbf{n} dA$$

where $\nabla \cdot \mathbf{j}_Q$ is called the *divergence* of $\mathbf{j}_Q$. In rectangular Cartesian coordinates

$$\nabla \cdot \mathbf{j}_Q = \frac{\partial}{\partial x} j_{Qx} + \frac{\partial}{\partial y} j_{Qy} + \frac{\partial}{\partial z} j_{Qz} \tag{11.39}$$

The divergence of a vector written in component form is often abbreviated as follows:

$$\frac{\partial}{\partial x} j_{Qx} + \frac{\partial}{\partial y} j_{Qy} + \frac{\partial}{\partial z} j_{Qz} \equiv \frac{\partial}{\partial x_i} j_{Qi} \tag{11.40}$$

In this notation it is assumed that a summation is carried out over all indices which appear twice in the same term; x_i, $i = 1,2,3$ stands for the three components (x,y,z) of the coordinate system. In this form, the divergence looks like the expression used in single-dimensional cases. In fact, the simplest examples usually suggest the proper form of more complicated cases.

11.3 THE BALANCE OF MASS

Let us start with the first of the three fluidlike quantities for which we have to obtain laws of balance, namely the amount of substance. The balance of amount of substance is a necessary prerequisite for formulating theories applicable to fluid or otherwise deformable media. If we wish to quantify convective currents associated with processes in open systems, we have to be able to write down the currents of amount of substance. For practical reasons, however, engineers commonly use mass as a substitute for amount of substance, and as long as there are no chemical reactions taking place inside the material, there is no problem in doing so. Therefore, we will use a formulation based on mass.

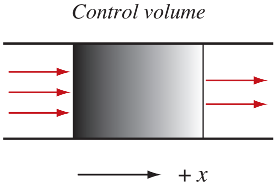

Figure 11.8: Simple one-dimensional flow with respect to an open and stationary control volume. Imagine a fluid flowing in the *x*-direction only.

In the previous section we introduced the concepts and tools needed to formulate the continuum forms of the laws of balance of fluidlike quantities. Starting with the integrated form of the balance of mass

$$\dot{m} = I_m \tag{11.41}$$

we can easily show how to obtain the appropriate local equation applicable to the continuous case. Let us apply this law to a stationary control volume of simple shape (Fig. 11.8) and assume the flow field to be one-dimensional. In this equation, m is the mass inside the control volume, while I_m is the net current of mass across the surface of the control volume. We shall replace the mass by the volume integral of the mass density, and the flux by the surface integral of the flux density, as in Equ.(11.26). With Equ.(11.34) this leads to

$$\frac{d}{dt}\int_{\mathcal{V}} \rho dV + \int_{\mathcal{A}} \rho v dA = 0 \tag{11.42}$$

If we use the divergence theorem for the surface integral and apply the time derivative

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8. For a derivation of the divergence theorem see Marsden and Weinstein (1985), Vol. III, p. 927.

to the integrand of the first integral, we obtain

$$\int_{\mathcal{V}} \frac{\partial \rho}{\partial t} dV + \int_{\mathcal{V}} \frac{\partial}{\partial x}(\rho v) dV = 0$$

or

$$\int_{\mathcal{V}} \left[\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v) \right] dV = 0$$

Since the integral must be zero for arbitrary volumes *V*, the last expression can only be satisfied if the terms in brackets are equal to zero:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v) = 0 \qquad \textbf{(11.43)}$$

You can easily apply the transformations to the more general three-dimensional case

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho v_i) = 0 \qquad \textbf{(11.44)}$$

or

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \qquad \textbf{(11.45)}$$

This looks very similar to the simpler expression. In contrast to Equ.(11.42) which is the integral form of the law of balance of mass, Equ.(11.43) and its counterpart in Equations (11.44) or (11.45) represent the local or differential form of this law. The balance of mass often is called the equation of continuity.

11.4 THE BALANCE OF ENTROPY

Entropy is a scalar quantity just like mass, so the derivation of the local form of the law of balance should lead to a result similar to what we have just seen. Consider as we did in Fig. 11.8, the flow of a fluid in the *x*-direction only. As far as entropy is concerned, we will include conductive and convective transports in the derivation, and production of entropy in irreversible processes. Sources of entropy from radiation, however, will be excluded here. The integral form of the equation of balance of entropy for the control volume in Fig. 11.8 then looks like

$$\dot{S} = I_{S,conv} + I_{S,cond} + \Pi_S \qquad \textbf{(11.46)}$$

If we introduce densities and current densities as in Section 11.2, the law becomes

$$\frac{d}{dt}\int_{\mathcal{V}} (\rho s) dV + \int_{\mathcal{A}} \left(s\rho v + j_S^{(c)} \right) dA = \int_{\mathcal{V}} \pi_S dV \qquad \textbf{(11.47)}$$

s is the *specific entropy* of the fluid, $j_S^{(c)}$ and π_S represent the conductive *entropy current density* and the *density of the entropy production rate*, respectively. Remember that we are dealing with a purely one-dimensional case. If we now apply the transformation of the surface integral, we obtain

$$\int_{\mathcal{V}} \left[\frac{\partial}{\partial t}(\rho s) + \frac{\partial}{\partial x}\left(s\rho v + j_S{}^{(c)} \right) - \pi_S \right] dV = 0$$

The expression in brackets must be zero, which yields the local form of the law of balance:

$$\frac{\partial}{\partial t}(\rho s) + \frac{\partial}{\partial x}\left(s\rho v + j_S{}^{(c)} \right) = \pi_S \tag{11.48}$$

The general three-dimensional case can be written in a form that looks just like the one derived for purely one-dimensional transports. Applying the divergence theorem to the generalized form of Equ.(11.47) yields

$$\frac{\partial}{\partial t}(\rho s) + \nabla \cdot \left(s\rho \mathbf{v} + \mathbf{j}_S{}^{(c)} \right) = \pi_S \tag{11.49}$$

or

$$\frac{\partial}{\partial t}(\rho s) + \frac{\partial}{\partial x_i}\left(s\rho v_i + j_{Si}{}^{(c)} \right) = \pi_S \tag{11.50}$$

Extending this result to include the effects of sources from radiation is pretty simple. How this is done will be demonstrated below for the case of momentum (remember that gravity leads to sources of momentum).

11.5 THE BALANCE OF MOMENTUM

Basically, the law of balance of momentum is derived analogously to what you have seen so far. While the fundamental ideas do not change, the current case can be rather complex if we try to deal with it in the most general form. It is therefore all the more important to discuss the simplest possible nontrivial case. Fortunately, purely one-dimensional flow of momentum is meaningful in physical terms, so let us deal with this case in some detail.

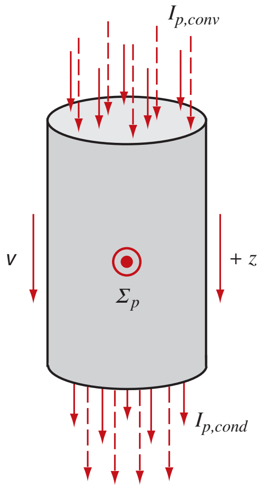

Figure 11.9: Flow lines depicting the convective and conductive transports of momentum are shown together with a source of momentum due to the interaction of the fluid with the gravitational field. The fluid is flowing downward leading to the convective downward flow of momentum together with the fluid (dashed lines). Since the material is under compression, momentum flows conductively in the positive direction (downward; solid lines). With the positive direction as chosen, the gravitational field supplies momentum to the fluid.

One-dimensional convective transport of momentum is a simple concept: if a fluid flows in one direction only, it carries only one single component of momentum. The case of one-dimensional conductive transport is just as well known. Let the direction of fluid flow define the spatial component we are talking about. Having the same component of momentum flowing through the fluid simply means that the material is under compression or tension in the same direction. A frictionless fluid flowing through a straight pipe demonstrates what we mean: the conductive momentum current density of the component parallel to the pipe's axis is the pressure of the fluid.

In addition to conductive and convective modes of transport, we will consider sources of momentum due to the interaction of the fluid with a field. If you imagine the fluid flowing through a vertical pipe (Fig. 11.9), the action of the gravitational field leads to the flow of momentum of the same (vertical) component directly into or out of the body.

If we collect the different terms, the integral equation of balance of momentum for the z-direction looks like

$$\dot{p} = I_{p,conv} + I_{p,cond} + \Sigma_p \tag{11.51}$$

where *p* stands for the *z*-component of momentum. As before, we introduce the proper densities and flux densities and obtain

$$\frac{d}{dt}\int_{\mathcal{V}}(\rho v)dV + \int_{\mathcal{A}}\left(\rho v v + j_p^{(c)}\right)dA = \int_{\mathcal{V}}\sigma_p dV \tag{11.52}$$

Now, we can apply the divergence theorem to this equation:

$$\int_{\mathcal{V}}\left[\frac{\partial}{\partial t}(\rho v) + \frac{\partial}{\partial x}\left(\rho v v + j_p^{(c)}\right) - \sigma_p\right]dV = 0$$

leading to the desired differential form of balance of momentum for the purely one-dimensional example discussed so far:

$$\frac{\partial}{\partial t}(\rho v) + \frac{\partial}{\partial x}\left(\rho v v + j_p^{(c)}\right) = \sigma_p \tag{11.53}$$

The general case requires two additional steps. First, for a component of momentum, we have to treat the momentum flux as a vector; this yields an equation similar to Equ.(11.49) for the component. Second, we have to write analogous equations for the other two components of momentum:

$$\begin{aligned}
\frac{\partial}{\partial t}(\rho v_x) + \nabla\cdot\left(\rho v_x \mathbf{v} + \mathbf{j}_{px}^{(c)}\right) &= \sigma_{px}\\
\frac{\partial}{\partial t}(\rho v_y) + \nabla\cdot\left(\rho v_y \mathbf{v} + \mathbf{j}_{py}^{(c)}\right) &= \sigma_{py}\\
\frac{\partial}{\partial t}(\rho v_z) + \nabla\cdot\left(\rho v_z \mathbf{v} + \mathbf{j}_{pz}^{(c)}\right) &= \sigma_{pz}
\end{aligned} \tag{11.54}$$

These three equations can be written as a single one using the momentum current tensor introduced in Footnote 7. While the result can be presented in a compact form, the actual equations are rather lengthy and difficult to read in their component form.

Let us briefly return to the meaning of the conductive momentum flux and the source term in Equ.(11.53). For a simple fluid, the purely one-dimensional case of conductive momentum transport describes the state of compression of that fluid. In other words, the current density is the pressure of the fluid:

$$j_p^{(c)} = P \tag{11.55}$$

The source term, on the other hand, arises as the result of the gravitational interaction. As described in Section 3.3, the gravitational field supplies momentum to the body, leading to a source rate, which in integrated form, must be equal to the weight of the body. The source density must therefore equal

$$\sigma_p = \rho g \tag{11.56}$$

which shows that the specific source rate f_p introduced in Equ.(11.23) is the gravitational field strength g. The influence of fields other than the gravitational field can be included in the same manner. Forces of this nature are called body forces.

11.6 THE MATERIAL DERIVATIVE AND LAWS OF BALANCE

The local form of the equations of balance derived above has a couple of features which need explaining. The derivatives occurring in relations such as Equ.(11.48) or Equ.(11.53) are partial derivatives, which means that, for example, the time derivative must be taken at a fixed position. This form is often called the *Eulerian form* of the partial differential equations describing the balance of fluidlike quantities. The second feature is related to the first: the equations explicitly contain convective currents.

It is possible to transform the laws of balance using the balance of mass and to obtain alternative forms which no longer contain the convective currents. As such, the resulting equations look as if they were written for closed systems for which convection does not play a role. Instead, there appears a combination of derivatives of the density of the quantity investigated, a combination which can be interpreted as a *material derivative*. Let us see how this happens.

Take as an example the simple law of balance of entropy in Equ.(11.48). If you take the derivative of some of the products occurring in the equation, you get

$$\rho\frac{\partial s}{\partial t}+s\frac{\partial \rho}{\partial t}+s\frac{\partial(\rho v)}{\partial x}+\rho v\frac{\partial s}{\partial x}+\frac{\partial j_s^{(c)}}{\partial x}=\pi_S$$

or

$$\rho\left[\frac{\partial s}{\partial t}+v\frac{\partial s}{\partial x}\right]+s\left[\frac{\partial \rho}{\partial t}+\frac{\partial(\rho v)}{\partial x}\right]+\frac{\partial j_s^{(c)}}{\partial x}=\pi_S$$

According to the law of balance of mass presented in Equ.(11.43), the term in the second pair of brackets must equal zero. Therefore, the transformed law of balance looks like

$$\rho\left[\frac{\partial s}{\partial t}+v\frac{\partial s}{\partial x}\right]+\frac{\partial j_s^{(c)}}{\partial x}=\pi_S \qquad \textbf{(11.57)}$$

The convective current density has disappeared. Introducing the operator

$$\frac{D}{Dt}=\frac{\partial}{\partial t}+v\frac{\partial}{\partial x} \qquad \textbf{(11.58)}$$

which is commonly called the *material time derivative* or the *substantial derivative*, Equ.(11.57) can be written as follows:

$$\rho\frac{Ds}{Dt}+\frac{\partial j_S^{(c)}}{\partial x}=\pi_S \qquad \textbf{(11.59)}$$

The time rate of change of the quantity s expressed by the material derivative is the one measured by someone carried along with the fluid rather than by someone at a fixed location.

11.7 THE ENERGY PRINCIPLE

The law of balance of energy should be considered separately. The reason for this is not that the energy principle is more important than any of the other fundamental laws but that we should again stress that energy is special in that it appears equally in all physical phenomena and not just in one special subject area. The formal expression of this idea was applied in Chapter 10, where the energy principle was understood to put restrictions upon the processes in question. It will be used again further below in Section 11.8, where the theory of thermodynamics of viscous heat-conducting fluids will be presented.

Since energy is exchanged in all types of physical processes, it is almost impossible, and certainly not realistic, to try to present a totally general form of the law of balance. The following discussion is in line with the area of applications considered here, namely the thermomechanics of nonreacting fluid systems.

11.7.1 Energy Density and Energy Current Densities

Consider again a fluid flowing through a control volume such as in Fig. 11.8, and let all transports be purely one-dimensional. In addition to mass, entropy, and momentum, energy is transported across the faces of the control volume, and just like the other quantities, it can also be stored in the system. Since energy cannot be produced, we will have to consider the density of energy in the fluid, energy density currents across the surface, and sources of energy due to radiative transports.

The energy density of a fluid. A fluid contains an amount of energy that depends upon its state, which in this case, can be described by temperature, pressure, and velocity. It is common to associate a part of the energy content with the state of motion of the material (i.e., the kinetic energy) while the rest is lumped together as the internal energy of the fluid. This distinction was made in Chapter 8 where we discussed simple applications of flow processes. The density of energy of the fluid is therefore written as the sum of two parts, the density of internal energy, and the density of kinetic energy. If we use instead the specific values of internal energy and of kinetic energy, the expression takes the following form:

$$\rho e = \rho\left(u + \frac{1}{2}v^2\right) \tag{11.60}$$

Here, e is the specific energy, while $u = e^{(i)}$ stands for the specific internal energy (intrinsic part of e). Naturally, the second term on the right-hand side represents the kinetic energy per mass. The energy of a fluid system can then be written as follows:

$$E = \int_{\mathcal{V}} \rho\left(u + \frac{1}{2}v^2\right)dV \tag{11.61}$$

Energy current densities. Energy can be carried into or out of a control volume across the surface of the system. Such processes are described in terms of currents. Since the exchange of energy may be the result of numerous different interactions, we should be specific and discuss only those phenomena which are important to our current theme. Other cases can be treated in analogy to what we do here. Since energy can be transferred convectively and conductively, we can say that

$$j_E = j_{E,conv} + j_{E,cond} \tag{11.62}$$

In general, these current densities are vectors. The convective transport is the result of the fluid carrying stored energy across the system boundary. We need the convective energy flux density to quantify this process; it can be expressed in terms of the specific energy and the flux of mass:

$$j_{E,conv} = \rho v e = \rho v\left(u + \frac{1}{2}v^2\right) \tag{11.63}$$

The conductive transport of energy presents a slightly more complicated problem, since we might have to consider all sorts of transfer processes. Limiting our attention to thermal and mechanical phenomena, however, leaves us with only two possibilities: energy may be either added or withdrawn together with entropy in heating and cooling, or it may flow across the system boundary as the result of the conductive exchange of momentum:

$$j_{E,cond} = j_{E,th} + j_{E,mech} \tag{11.64}$$

The former possibility gets short treatment; since we shall try to establish the relationship between transports of entropy and of energy, we cannot say more about this case so we simply introduce a thermal energy current density. The second term in this equation, on the other hand, is well known from mechanics. The exchange of energy is directly tied to the conductive flow of momentum, and to the speed of the fluid at the surface of the system:

$$j_{E,mech} = v j_p^{(c)} \tag{11.65}$$

In three dimensions, a component of the energy flux density vector is obtained for each component of momentum by calculating the scalar product of the momentum current vector and the velocity. Adding up all the terms introduced so far yields the desired expression for the energy current density:

$$j_E = \rho v\left(u + \frac{1}{2}v^2\right) + v j_p^{(c)} + j_{E,th} \tag{11.66}$$

As mentioned before, this equation has to be changed or extended if other processes are to be taken into consideration.

The total energy flux with respect to the control volume in Fig. 11.8 is obtained by integrating the expression in Equ.(11.66) over the surface elements perpendicular to the direction of flow:

$$I_E = -\int_{\mathcal{A}}\left[\rho v\left(u + \frac{1}{2}v^2\right) + v j_p^{(c)} + j_{E,th}\right]dA \tag{11.67}$$

Sources of energy. Energy can be directly supplied to the interior of a body or a control volume as a consequence of its interaction with fields. Three cases of interest to us are the supply of energy together with momentum if we include the action of a gravitational field; sources of energy due to the absorption of electromagnetic radiation;

and sources of energy such as those related to nuclear decay or chemical reactions inside the system. Describing these effects calls for introducing an energy supply density such that

$$\Sigma_E = \int_{\mathcal{V}} \sigma_E \, dV \qquad \textbf{(11.68)}$$

Gravitational interaction and absorption of radiation lead to a specific expression for the source density, namely

$$\sigma_E = \rho\left(f_p v + r\right) \qquad \textbf{(11.69)}$$

where $f_p = g$ is the specific source rate of momentum (the specific body force) and r denotes the specific rate of absorption of energy together with radiation.

11.7.2 The Balance of Energy

Writing down the law of balance of energy as it applies to a fairly general case of the thermomechanics of fluid systems, is as simple as the examples we have seen before. The integral statement

$$\dot{E} = I_E + \Sigma_E \qquad \textbf{(11.70)}$$

can be written using the densities and the current densities:

$$\begin{aligned} \frac{d}{dt}\int_{\mathcal{V}} \rho\left(u + \frac{1}{2}v^2\right) dV + \int_{\mathcal{A}} \left[\rho v\left(u + \frac{1}{2}v^2\right) + v j_p{}^{(c)} + j_{E,th}\right] dA & \\ = \int_{\mathcal{V}} \rho\left(f_p v + r\right) dV & \end{aligned} \qquad \textbf{(11.71)}$$

Applying the integral transformation to the surface integral, collecting all the terms on one side, and noting that the resulting volume integral must vanish identically, yields the local form of the law of balance of energy:

$$\frac{\partial}{\partial t}\rho\left(u + \frac{1}{2}v^2\right) + \frac{\partial}{\partial x}\left[\rho v\left(u + \frac{1}{2}v^2\right) + v j_p{}^{(c)} + j_{E,th}\right] = \rho\left(f_p v + r\right) \qquad \textbf{(11.72)}$$

Together with the laws of balance derived above for mass, entropy, and momentum, this equation will furnish the starting point for the development of our example of continuum thermodynamics in Section 11.8.

11.7.3 The Balance of Energy in the Material Form

As mentioned in Section 11.6, the local equations of balance are often written using the material derivative, Equ.(11.58), in which case they look like laws of balance written for a particular body, i.e., for a closed system. Let us first motivate this particular form for supply-free processes before attempting a derivation.

Imagine following a fluid in motion. For observers flowing along with a particular body, the momentum of the material is always zero and, as a corollary, the kinetic energy vanishes; they see only the internal energy of the fluid. The exchange of energy with the environment takes two forms. The momentum flowing through the body does so with or against a gradient of the potential of motion, i.e., with or against the gradient of the velocity at the location of the body. The rate per volume at which energy is released is equal to the product of the current density of momentum and the gradient of the velocity. A similar result holds for the thermal interaction; only here we do not know the relationship between the flux of energy and the flux of entropy. The rate of release of energy per volume in the body is equal to the gradient of the energy flux density. Adding up the terms should yield

$$\rho \frac{Du}{Dt} + j_p^{(c)} \frac{\partial v}{\partial x} + \frac{\partial j_{E,th}}{\partial x} = 0 \tag{11.73}$$

The second term in this equation is called the *stress power*.

This result is a consequence of Equ.(11.72), and the laws of balance of mass and of momentum Equations (11.43) and (11.53); remember that we do not include any of the source terms. In a first step, the law of balance of energy becomes

$$\begin{aligned} &\rho \frac{\partial u}{\partial t} + u \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial t}\left(\frac{1}{2}\rho v^2\right) + \rho v \frac{\partial u}{\partial x} + u \frac{\partial(\rho v)}{\partial x} \\ &\qquad + \frac{\partial}{\partial x}\left[\rho v\left(\frac{1}{2}v^2\right)\right] + \frac{\partial}{\partial x}\left(v j_p^{(c)}\right) + \frac{\partial j_{E,th}}{\partial x} = 0 \end{aligned}$$

Together, the second and the fifth terms vanish because of the law of balance of mass, while the first and the fourth terms yield the product of the density and the material derivative of the internal energy. Therefore we have

$$\rho \frac{Du}{Dt} + j_p^{(c)} \frac{\partial v}{\partial x} + \frac{\partial j_{E,th}}{\partial x} + \left\{ \frac{\partial}{\partial t}\left(\frac{1}{2}\rho v^2\right) + \frac{\partial}{\partial x}\left[\rho v\left(\frac{1}{2}v^2\right)\right] + v \frac{\partial j_p^{(c)}}{\partial x} \right\} = 0$$

If we can show that the expression inside the braces in this expression is zero, then the proof of Equ.(11.73) is complete. Now, the spatial derivative of the momentum current density can be replaced using the law of balance of momentum:

$$\begin{aligned} &\frac{\partial}{\partial t}\left(\frac{1}{2}\rho v^2\right) + \frac{\partial}{\partial x}\left[\rho v\left(\frac{1}{2}v^2\right)\right] + v \frac{\partial j_p^{(c)}}{\partial x} \\ &\qquad = \frac{\partial}{\partial t}\left(\frac{1}{2}\rho v^2\right) + \frac{\partial}{\partial x}\left[\rho v\left(\frac{1}{2}v^2\right)\right] + v\left[-\frac{\partial}{\partial t}(\rho v) - \frac{\partial}{\partial x}(\rho v v)\right] \end{aligned}$$

After some lengthy algebra, we find that this expression is equal to

$$-\frac{1}{2}v^2\left(\frac{\partial \rho}{\partial t} + v\frac{\partial \rho}{\partial x} + \rho\frac{\partial v}{\partial x}\right)$$

This quantity vanishes because of the law of balance of mass. Naturally, for the three-dimensional case, the derivation is more involved, but the result still holds in a form similar to the one stated above.

11.8 THERMODYNAMICS OF A VISCOUS HEAT CONDUCTING FLUID

The bulk of engineering work in the fields of fluid dynamics and heat transfer is built upon the basis of the theory of heat-conducting viscous fluids, the subject we will discuss in this section. Except for constructing the constitutive laws applicable to the field, we have already done most of the preparations necessary for the following development. We must only assemble the parts and derive the consequences of the assumptions, much like we did for the uniform viscous fluid in Chapter 10. If the following lines look forbidding at first, keep in mind that it is the amount of algebra needed which creates this impression. The results can be understood intuitively in terms of what we have learned in the previous chapters.

The assumptions which the theory is based upon can be divided into three groups. The first, the laws of balance of mass, entropy, momentum, and energy, has been discussed above; we only must assemble them in the form which applies to our case. The second is made up of the preliminary expressions for the constitutive laws which will be introduced in Section 11.8.2 and the third group deals with the assumption of ideal walls which we will not go into again (see Section 10.1 for more details).

11.8.1 The Laws of Balance

The laws of balance used in the field of nonreactive heat-conducting viscous fluids are those of mass, entropy, momentum, and energy. For the following derivation, we will stay with the simple one-dimensional case discussed in the previous sections. For source-free processes, the appropriate forms of the first three laws are

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v) = 0 \\
&\frac{\partial}{\partial t}(\rho s) + \frac{\partial}{\partial x}\left(s \rho v + j_S{}^{(c)}\right) = \pi_S \\
&\frac{\partial}{\partial t}(\rho v) + \frac{\partial}{\partial x}\left(\rho v v + j_p{}^{(c)}\right) = 0
\end{aligned} \tag{11.74}$$

while the balance of energy looks as follows

$$\frac{\partial}{\partial t}\left[\rho\left(u + \frac{1}{2}v^2\right)\right] + \frac{\partial}{\partial x}\left[\rho v\left(u + \frac{1}{2}v^2\right) + v j_p{}^{(c)} + j_{E,th}\right] = 0 \tag{11.75}$$

In component notation for three dimensions, the equations of balance for the three main fluidlike quantities are as follows:

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho v_j) = 0 \\
&\frac{\partial}{\partial t}(\rho s) + \frac{\partial}{\partial x_j}\left(s \rho v_j + j_{Sj}{}^{(c)}\right) = \pi_S \\
&\frac{\partial}{\partial t}(\rho v_i) + \frac{\partial}{\partial x_j}\left(\rho v_i v_j + j_{pij}{}^{(c)}\right) = 0
\end{aligned} \tag{11.76}$$

The balance of energy takes the form

$$\frac{\partial}{\partial t}\left[\rho\left(u+\frac{1}{2}v^2\right)\right]+\frac{\partial}{\partial x_j}\left[\rho v_j\left(u+\frac{1}{2}v^2\right)+v_i\, j_{pij}{}^{(c)}+j_{E,th,j}\right]=0 \tag{11.77}$$

Remember that we have to sum over the indices which appear twice in an expression ($j = 1,2,3$).

As you know from all the examples in the previous chapters, equations of balance do not solve a problem by themselves. Moreover, they contain as their most important quantities those which are often not accessible to measurement. If we wish to specify the condition of a fluid in terms of density, velocity, and temperature at different points in space for different times, i.e., if we wish to obtain the functions $\rho(\mathbf{x},t)$, $\mathbf{v}(\mathbf{x},t)$, and $T(\mathbf{x},t)$, we will obviously have to eliminate quantities such as entropy and energy from the equations. This goal is achieved if we know the proper constitutive laws with whose help the equations of balance can be transformed into field equations for the measurable quantities.

11.8.2 Constitutive Relations for a Navier-Stokes-Fourier Fluid

In this section we will present the constitutive laws which govern the behavior of viscous heat-conducting fluids in a strongly simplified form. It is possible to include all the interesting physical effects in the purely one-dimensional case. This reduces the complexity of the calculations considerably. We will need preliminary forms of the constitutive laws for the specific entropy and energy and for the flux densities of entropy, momentum, and energy (for the case of heating). A suitable thermal equation of state must be added to these.[9]

In many instances, gradients of temperature and velocity in fluids can be assumed to be small, which leads to particularly simple forms of the constitutive laws with only linear dependence on the gradients. We shall assume that

$$s = s(\rho,T) \tag{11.78}$$

and

$$u = u(\rho,T) \tag{11.79}$$

for the specific quantities, and

$$\begin{aligned} j_p{}^{(c)} &= P(\rho,T) - \mu'(\rho,T)\frac{\partial v}{\partial x} \\ j_S{}^{(c)} &= -k_S(\rho,T)\frac{\partial T}{\partial x} \\ j_{E,th} &= -\beta(\rho,T)\frac{\partial T}{\partial x} \end{aligned} \tag{11.80}$$

for the fluxes of momentum, entropy, and energy (for heating).[10] Here, μ' is a viscosity

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[9] For more details on the proper constitutive laws, you should turn to books such as those by Müller (1985) and Malvern (1969).

which may include the bulk viscosity with the normal viscosity μ of the fluid, while k_S is the thermal conductivity with respect to entropy (i.e., the entropy conductivity);[11] β is a function that will be related to k_S later. We have used constitutive expressions of these or similar forms before for the simple materials treated in previous chapters. Remember that the terms involving gradients of temperature or velocity are the local forms of our simpler expressions for conductive transports: a conductive flow is one that depends upon the difference of its own potential. The first equation, Equ.$(11.80)_1$, reminds us of the special pressure law used in Section 10.1.1 where we dealt with a uniform viscous fluid. Velocity gradients in one dimension mean that the fluid is either being compressed or expanded, leading to viscous effects. The other two expressions, Equations $(11.80)_{2,3}$, are Fourier's law of heat conduction.

11.8.3 Evaluation of the Energy Principle

We wish to be able to derive more detailed results about the constitutive laws and quantities of a Navier-Stokes-Fourier fluid. As you remember, the laws of balance serve as restrictions upon these relations. In particular, all processes must satisfy the energy principle in addition to the laws of balance of amount of substance (mass), entropy, and momentum. In Chapter 10, the approach using Lagrange multipliers was introduced; we will now use it for the present case. The laws of balance are satisfied simultaneously if and only if the following relation holds:

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10. Actually, the preliminary forms are slightly more complicated. First, one exploits the principle of material frame indifference and representation theorems for isotropic functions to obtain rather general expressions for the constitutive laws (Müller, p. 4–7). These expressions are linearized, leading to

$$
\begin{aligned}
&s = s(\rho,T) + a(\rho,T)d_{ii}\\
&u = u(\rho,T) + b(\rho,T)d_{ii}\\
&j_{pij}{}^{(c)} = P(\rho,T)\delta_{ij} - \lambda(\rho,T)d_{kk}\delta_{ij} - 2\mu(\rho,T)d_{ij}\\
&j_S{}^{(c)} = -k_s(\rho,T)\frac{\partial T}{\partial x}\\
&j_{E,th} = -\beta(\rho,T)\frac{\partial T}{\partial x}
\end{aligned}
$$

for the three-dimensional case of the Navier-Stokes-Fourier fluid. When the equations of balance are exploited, the functions *a* and *b* turn out to be equal to zero, meaning that the entropy and the density take the same form in equilibrium as in nonsteady-state processes. To simplify the derivation, we have omitted the terms relating to the gradient of velocity from Equ.(11.78). Equ.$(11.80)_1$ is the purely one-dimensional version of the expression for the stress tensor for nonvanishing bulk viscosity, where

$$d_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)$$

is the symmetric part of the velocity gradient tensor, and λ and μ are two independent parameters characterizing the influence of viscosity of the fluid.

$$\begin{aligned}&\frac{\partial}{\partial t}\left[\rho\left(u+\frac{1}{2}v^2\right)\right]+\frac{\partial}{\partial x}\left[\rho v\left(u+\frac{1}{2}v^2\right)+v\,j_p{}^{(c)}+j_{E,th}\right]\\&-\lambda^\rho\left[\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial x}(\rho v)\right]-\lambda^S\left[\frac{\partial}{\partial t}(\rho s)+\frac{\partial}{\partial x}\left(s\rho v+j_S{}^{(c)}\right)-\pi_S\right]\\&-\lambda^v\left[\frac{\partial}{\partial t}(\rho v)+\frac{\partial}{\partial x}\left(\rho v v+j_p{}^{(c)}\right)\right]=0\end{aligned} \tag{11.81}$$

This expression is obtained by multiplying each of the equations of balance of mass, entropy, and momentum by its own Lagrange multiplier, which here are called λ^ρ, λ^S, and λ^v, respectively, and then subtracting them from the energy principle Equ.(11.77). For the following calculations, note that the constitutive quantities in the laws of balance are functions of ρ, T, dT/dx, and dv/dx. You can verify this by looking at Equations (11.78) and (11.80). We should now calculate the derivatives with respect to time and to position in Equ.(11.81), keeping in mind the dependencies just mentioned. This yields a long expression[12] with terms containing the derivatives

$$\frac{\partial v}{\partial t}\ ,\ \frac{\partial^2 v}{\partial x^2}\ ,\ \frac{\partial\rho}{\partial t}\ ,\ \frac{\partial\rho}{\partial x}\ ,\ \frac{\partial T}{\partial t}\ ,\ \frac{\partial^2 T}{\partial x^2}\ ,\ \text{and}\ \frac{\partial T}{\partial x}\ ,\ \frac{\partial v}{\partial x}$$

(If we had included the terms that depend upon the gradient of velocity in the constitutive expressions for specific entropy and energy (Footnote 10), the mixed derivative of the velocity with respect to time and position would also need to be taken into account.) While terms containing the first six of these are expressly linear in these derivatives (they do not occur again in the terms multiplying them), this is not true for the last two derivatives, since these are among the list of independent variables of the constitutive quantities. We separately assemble all the terms that are dependent upon the derivatives listed above.[13] Noting that the expressions multiplying the first six of the derivatives must vanish identically (otherwise the expression in Equ.(11.81) may be violated), we obtain six conditions which must be satisfied by the fluid, plus one re-

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11. The bulk viscosity is defined as

$$\kappa=\lambda+\frac{2}{3}\mu$$

where λ and μ have been introduced in the constitutive relations of the Navier-Stokes fluid in Footnote 10. In terms of the deviators

$$j_{pij}{}'=j_{pij}-P^*\delta_{ij}\quad,\quad d_{ij}{}'=d_{ij}-\frac{1}{3}d_{kk}\delta_{ij}$$

the (conductive) momentum current can be written as follows:

$$j_{pij}{}'=-2\mu\,d_{ij}{}'\quad,\quad P^*=P-\kappa\,d_{kk}$$

(see Malvern (1967), p. 299). The pressure P^* includes a bulk viscosity term in addition to the pressure P in equilibrium. For fluids with vanishing bulk viscosity, the pressure term to be used is the normal pressure, and the viscosity of a "one-dimensional" gas depends only upon the normal viscosity μ.

sidual equation containing the rate of production of entropy; the second of these is identical to the first, so we have only five conditions:

$$\begin{aligned}
&\nu = \lambda^{v} \\
&\rho \frac{\partial u}{\partial \rho} + u - \frac{1}{2}\nu^2 - \lambda^{\rho} - \lambda^{S} s - \lambda^{S} \rho \frac{\partial s}{\partial \rho} = 0 \\
&\frac{\partial j_E}{\partial \rho} - \lambda^{S} \frac{\partial {j_S}^{(c)}}{\partial \rho} = 0 \\
&\frac{\partial u}{\partial T} - \lambda^{S} \frac{\partial s}{\partial T} = 0 \\
&\frac{\partial j_E}{\partial T_{,x}} - \lambda^{S} \frac{\partial {j_S}^{(c)}}{\partial T_{,x}} = 0
\end{aligned} \tag{11.82}$$

and the following residual equation involving the gradients of temperature and velocity:

$$\begin{aligned}
&\frac{\partial T}{\partial x}\left\{\frac{\partial j_E}{\partial T} - \lambda^{S} \frac{\partial {j_S}^{(c)}}{\partial T}\right\} \\
&\qquad + \frac{\partial \nu}{\partial x}\left\{\rho\left(u - \frac{1}{2}\nu^2 - \lambda^{\rho} - \lambda^{S} s\right) + {j_p}^{(c)}\right\} + \lambda^{S} \pi_S = 0
\end{aligned} \tag{11.83}$$

This relation will be used to determine the rate of production of entropy as a consequence of heat conduction and of viscosity.

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[12] There are essentially four parts associated with the four laws of balance included in the combined expression of Equ.(11.81). Together they read:

$$\begin{aligned}
&\rho \frac{\partial u}{\partial \rho}\frac{\partial \rho}{\partial t} + \rho \frac{\partial u}{\partial T}\frac{\partial T}{\partial t} + u \frac{\partial \rho}{\partial t} + \rho \nu \frac{\partial \nu}{\partial t} + \frac{1}{2}\nu^2 \frac{\partial \rho}{\partial t} + \rho \nu \frac{\partial u}{\partial \rho}\frac{\partial \rho}{\partial x} + \rho \nu \frac{\partial u}{\partial T}\frac{\partial T}{\partial x} + u \nu \frac{\partial \rho}{\partial x} \\
&+\rho \nu^2 \frac{\partial \nu}{\partial x} + \nu \frac{1}{2}\nu^2 \frac{\partial \rho}{\partial x} + \rho\left(u + \frac{1}{2}\nu^2\right)\frac{\partial \nu}{\partial x} + {j_p}^{(c)} \frac{\partial \nu}{\partial x} + \nu \frac{\partial {j_p}^{(c)}}{\partial \rho}\frac{\partial \rho}{\partial x} + \nu \frac{\partial {j_p}^{(c)}}{\partial T}\frac{\partial T}{\partial x} \\
&+\nu \frac{\partial {j_p}^{(c)}}{\partial \nu_{,x}}\frac{\partial^2 \nu}{\partial x^2} + \frac{\partial j_E}{\partial \rho}\frac{\partial \rho}{\partial x} + \frac{\partial j_E}{\partial T}\frac{\partial T}{\partial x} + \frac{\partial j_E}{\partial T_{,x}}\frac{\partial^2 T}{\partial x^2} \\
&-\lambda^{\rho}\left[\frac{\partial \rho}{\partial t} + \rho \frac{\partial \nu}{\partial x} + \nu \frac{\partial \rho}{\partial x}\right] \\
&-\lambda^{S}\left[s \frac{\partial \rho}{\partial t} + \rho \frac{\partial s}{\partial \rho}\frac{\partial \rho}{\partial t} + \rho \frac{\partial s}{\partial T}\frac{\partial T}{\partial t} + s \nu \frac{\partial \rho}{\partial x} + s \rho \frac{\partial \nu}{\partial x} + \rho \nu \frac{\partial s}{\partial \rho}\frac{\partial \rho}{\partial x} + \rho \nu \frac{\partial s}{\partial T}\frac{\partial T}{\partial x}\right. \\
&\qquad\qquad \left. + \frac{\partial {j_S}^{(c)}}{\partial \rho}\frac{\partial \rho}{\partial x} + \frac{\partial {j_S}^{(c)}}{\partial T}\frac{\partial T}{\partial x} + \frac{\partial {j_S}^{(c)}}{\partial T_{,x}}\frac{\partial^2 T}{\partial x^2} - \pi_S\right] \\
&-\lambda^{v}\left[\rho \frac{\partial \nu}{\partial t} + \nu \frac{\partial \rho}{\partial t} + 2\rho \nu \frac{\partial \nu}{\partial x} + \nu^2 \frac{\partial \rho}{\partial x} + \frac{\partial {j_p}^{(c)}}{\partial \rho}\frac{\partial \rho}{\partial x} + \frac{\partial {j_p}^{(c)}}{\partial T}\frac{\partial T}{\partial x} + \frac{\partial {j_p}^{(c)}}{\partial \nu_{,x}}\frac{\partial^2 \nu}{\partial x^2}\right]
\end{aligned}$$

Here, $T_{,x}$ and $\nu_{,x}$ are the gradients of temperature and velocity, respectively.

11.8.4 Determination of the Lagrange Multipliers

A first look at Equ.$(11.82)_1$ tells us that the Lagrange multiplier associated with the equation of balance of momentum is equal to the velocity, a result which should not surprise us at all: the velocity is the potential of motion.

Next, we are going to introduce the constitutive expressions for the fluxes of entropy and of energy in heating, Equations $(11.80)_{2,3}$, into Equ.$(11.82)_5$. This yields a relation between the conductivity and the factor β:

$$\lambda^S k_S = \beta$$

which tells us that the Lagrange multiplier associated with entropy may depend only upon density and temperature. It also yields an equivalent relation between the fluxes themselves. You can introduce this latter relation in Equ.$(11.82)_3$ which leads to the following result:

---

13. After collecting the different terms, the expression in Footnote 12 becomes

$$\begin{aligned}
&\frac{\partial v}{\partial t}\left\{v\rho-\lambda^{v}\rho\right\}+\frac{\partial^2 v}{\partial x^2}\left\{v\frac{\partial j_p{}^{(c)}}{\partial v_{,x}}-\lambda^{v}\frac{\partial j_p{}^{(c)}}{\partial v_{,x}}\right\}+\\
&\frac{\partial\rho}{\partial t}\left\{\rho\frac{\partial u}{\partial\rho}+u+\frac{1}{2}v^2-\lambda^{\rho}-\lambda^{S}s-\lambda^{S}\rho\frac{\partial s}{\partial\rho}-\lambda^{v}v\right\}+\\
&\frac{\partial\rho}{\partial x}\left\{\rho v\frac{\partial u}{\partial\rho}+uv+v\frac{1}{2}v^2+v\frac{\partial j_p{}^{(c)}}{\partial\rho}+\frac{\partial j_E}{\partial\rho}-\lambda^{\rho}v\right.\\
&\qquad\qquad\left.-\lambda^{S}\left[sv+\rho v\frac{\partial s}{\partial\rho}+\frac{\partial j_s{}^{(c)}}{\partial\rho}\right]-\lambda^{v}\left[v^2+\frac{\partial j_p{}^{(c)}}{\partial\rho}\right]\right\}+\\
&\frac{\partial T}{\partial t}\left\{\rho\frac{\partial u}{\partial T}-\lambda^{S}\rho\frac{\partial s}{\partial T}\right\}+\frac{\partial^2 T}{\partial x^2}\left\{\frac{\partial j_E}{\partial T_{,x}}-\lambda^{S}\frac{\partial j_s{}^{(c)}}{\partial T_{,x}}\right\}+\\
&\frac{\partial T}{\partial x}\left\{\rho v\frac{\partial u}{\partial T}+v\frac{\partial j_p{}^{(c)}}{\partial T}+\frac{\partial j_E}{\partial T}-\lambda^{S}\left[\rho v\frac{\partial s}{\partial T}+\frac{\partial j_s{}^{(c)}}{\partial T}\right]-\lambda^{v}\frac{\partial j_p{}^{(c)}}{\partial T}\right\}+\\
&\frac{\partial v}{\partial x}\left\{\rho v^2+\rho\left(u+\frac{1}{2}v^2\right)+j_p{}^{(c)}-\lambda^{\rho}\rho-\lambda^{S}s\rho-\lambda^{v}2\rho v\right\}+\lambda^{S}\pi_s=0
\end{aligned}$$

Each of the first six expressions in braces must vanish; otherwise Equ.(11.81) may be violated. This leaves the residual equation

$$\begin{aligned}
&\frac{\partial T}{\partial x}\left\{\rho v\frac{\partial u}{\partial T}+v\frac{\partial j_p{}^{(c)}}{\partial T}+\frac{\partial j_E}{\partial T}-\lambda^{S}\left[\rho v\frac{\partial s}{\partial T}+\frac{\partial j_S{}^{(c)}}{\partial T}\right]-\lambda^{v}\frac{\partial j_p{}^{(c)}}{\partial T}\right\}+\\
&\frac{\partial v}{\partial x}\left\{\rho v^2+\rho\left(u+\frac{1}{2}v^2\right)+j_p{}^{(c)}-\lambda^{\rho}\rho-\lambda^{S}s\rho-\lambda^{v}2\rho v\right\}+\lambda^{S}\pi_s=0
\end{aligned}$$

which will let us calculate the rate of production of entropy as a consequence of conduction of heat and viscosity.

$$\frac{\partial j_E}{\partial \rho} - \lambda^S \frac{\partial}{\partial \rho}\left(\frac{1}{\lambda^S} j_E\right) = 0 \quad \Rightarrow \quad \frac{\partial \lambda^S}{\partial \rho} = 0$$

This proves that the Lagrange multiplier may be a function only of temperature, and we have

$$j_E = \lambda^S(T) j_S{}^{(c)} \tag{11.84}$$

The residual equation now takes the following form:

$$\lambda^S \pi_S = -j_S{}^{(c)} \frac{d\lambda^S}{dT}\frac{\partial T}{\partial x} - \frac{\partial v}{\partial x}\left\{\rho\left(u - \frac{1}{2}v^2 - \lambda^\rho - \lambda^S s\right) + j_p{}^{(c)}\right\} \tag{11.85}$$

This result has important consequences. Introducing the constitutive law for the flux density of entropy and for the current density of momentum yields

$$\lambda^S \pi_S = k_S \frac{d\lambda^S}{dT}\frac{\partial T}{\partial x}\frac{\partial T}{\partial x} - \rho\left(u - \frac{1}{2}v^2 + \frac{P}{\rho} - \lambda^\rho - \lambda^S s\right)\frac{\partial v}{\partial x} + \mu' \frac{\partial v}{\partial x}\frac{\partial v}{\partial x}$$

In equilibrium, where the gradients of temperature and of velocity are zero, the rate of production of entropy will vanish. Moreover, for the rate of production of entropy to be minimal in equilibrium, its derivatives with respect to the gradients must vanish:

$$\left.\frac{\partial \pi_S}{\partial T_{,x}}\right|_E = 0 \quad \text{and} \quad \left.\frac{\partial \pi_S}{\partial v_{,x}}\right|_E = 0$$

(*E* stands for equilibrium). The first condition is satisfied identically, while the latter delivers an interesting relation for the Lagrange multiplier associated with mass:

$$\lambda^\rho = u - \frac{1}{2}v^2 + \frac{P}{\rho} - \lambda^S s \tag{11.86}$$

As you may have noted, the Lagrange multiplier belonging to mass (amount of substance) already looks very similar to the chemical potential of the simple fluids discussed in Chapters 6 and 8.

11.8.5 Determination of the Lagrange Multiplier for Entropy

If we manage to determine the multiplier associated with entropy, the essential results of this section will have been derived. We shall know the relation (11.84) between flux densities of entropy and of energy in heating; the expression (11.85) for the rate of production of entropy; and the Lagrange multiplier for mass, Equ.(11.86), which is indeed going to tell us that the latter is the chemical potential.

The derivation roughly goes as follows. We now use the condition of existence of ideal walls. Analogous to what we did in Section 10.1.4, we derive the result that for two fluids separated by an ideal wall the Lagrange multiplier must be equal:

$$\lambda_{\text{I}}^S(T) = \lambda_{\text{II}}^S(T)$$

This means that the Lagrange multiplier is a universal function; i.e., it must be the same for different Navier-Stokes-Fourier fluids.

We can derive an expression for the rate of change of the specific entropy by combining Equ.(11.82)$_2$ and Equ.(11.82)$_4$. Taking into consideration the result derived in Equ.(11.86) we arrive at

$$\dot{s} = \frac{1}{\lambda^S}\left(\frac{\partial u}{\partial \rho} - \frac{P}{\rho^2}\right)\dot{\rho} + \frac{1}{\lambda^S}\frac{\partial u}{\partial T}\dot{T} \tag{11.87}$$

Since we assume the functions to be sufficiently smooth, this implies an integrability condition of the form

$$\frac{\partial}{\partial T}\left\{\frac{1}{\lambda^S}\left(\frac{\partial u}{\partial \rho} - \frac{P}{\rho^2}\right)\right\} = \frac{\partial}{\partial \rho}\left\{\frac{1}{\lambda^S}\frac{\partial u}{\partial T}\right\}$$

Keep in mind that the Lagrange multiplier depends only upon temperature; you can now derive the following differential equation for the multiplier:

$$\frac{1}{\lambda^S}\frac{d\lambda^S}{dT} = \frac{\partial}{\partial T}\left(\frac{P}{\rho^2}\right)\left(\frac{P}{\rho^2} - \frac{\partial u}{\partial \rho}\right)^{-1} \tag{11.88}$$

Since this relation must hold for all types of fluids, it should also hold for the ideal gas, in which case the right-hand side turns out to be equal to the inverse of the ideal gas temperature. Therefore, we finally have the important result

$$\lambda^S = T \tag{11.89}$$

As in previous examples of materials, the thermal potential is the ideal gas temperature for the Navier-Stokes-Fourier fluid as well.

11.8.6 The Results for Navier-Stokes-Fourier Fluids

We can now assemble the results of the theory. Expressions for the relation between fluxes of entropy and energy, for the rate of production of entropy, and for the Lagrange multiplier for mass (i.e., the chemical potential) can be written in their final form:

$$j_{E,th} = T\, j_S^{(c)} \tag{11.90}$$

$$\pi_S = \frac{1}{T}k_S\frac{\partial T}{\partial x}\frac{\partial T}{\partial x} + \frac{1}{T}\mu'\frac{\partial v}{\partial x}\frac{\partial v}{\partial x} \tag{11.91}$$

$$\mu_m = u - \frac{1}{2}v^2 + \frac{P}{\rho} - T\,s \tag{11.92}$$

Equ.(11.91) also shows that the viscosity may not be a negative quantity (the rate of production of entropy should be positive even if no conduction of heat is present), and

Equ.(11.90) lets us calculate the factor β and the energy current due to conduction:

$$\beta = k_E = T\,k_S \quad \Rightarrow \quad j_{E,th} = -k_E\,\frac{\partial T}{\partial x} \tag{11.93}$$

The index *m* in Equ.(11.92) reminds us that the chemical potential of the fluid has been written for mass instead of for amount of substance. Multiplying the expression by the molar mass delivers the result we know from the treatment of uniform fluids in Chapter 8. From Equ.(11.87), we can also derive the Gibbs Fundamental Form for the heat-conducting viscous fluids investigated here. Interestingly, it is the same as the one known from the theory of uniform ideal fluids:

$$\dot{u} = T\,\dot{s} + \frac{P}{\rho^2}\,\dot{\rho} \tag{11.94}$$

Here, it is written using the density of the fluid instead of the volume of a particular body. The fact that some results look the same for reversible and for irreversible fluids is often interpreted as meaning that Navier-Stokes-Fourier fluids do not deviate much from equilibrium (a condition called *local thermodynamic equilibrium*). We normally get such results for materials having linear constitutive relations like Fourier's law or Newton's law of viscosity. A simple case of where all of this does not hold is the example of heat conduction with inductive behavior.

11.8.7 The Thermal Energy Equation for the One-Dimensional NS Fluid

It is common to present the balance of energy in the material form with the constitutive quantities introduced. The resulting relation is called the thermal energy equation. If you start with Equ.(11.73) and use the constitutive relations in the form

$$\begin{aligned} &u = u(\rho,T) \\ &j_p^{(c)} = P(\rho,T) - \mu'(\rho,T)\frac{\partial v}{\partial x} \\ &j_{E,th} = -k_E(\rho,T)\frac{\partial T}{\partial x} \end{aligned}$$

then the balance of energy becomes

$$\rho\frac{Du(\rho,T)}{Dt} + \left(P(\rho,T) - \mu'(\rho,T)\frac{\partial v}{\partial x}\right)\frac{\partial v}{\partial x} + \frac{\partial}{\partial x}\left(-k_E(\rho,T)\frac{\partial T}{\partial x}\right) = 0$$

or

$$\rho\left[\frac{\partial u}{\partial \rho}\frac{D\rho}{Dt} + \frac{\partial u}{\partial T}\frac{DT}{Dt}\right] + P\frac{\partial v}{\partial x} - \mu'\left(\frac{\partial v}{\partial x}\right)^2 - \frac{\partial}{\partial x}\left(k_E\,\frac{\partial T}{\partial x}\right) = 0 \tag{11.95}$$

It is interesting to specialize this result to an incompressible fluid. Because of this new condition, the first term with the rate of change of the density disappears and so do the terms involving pressure and viscosity. (In one dimension, the speed of the incompressible fluid may not change with position.) If we assume constant fluid properties, we finally get

$$\rho c\left(\frac{\partial T}{\partial t}+v\frac{\partial T}{\partial x}\right)-k_E\,\frac{\partial^2 T}{\partial x^2}=0 \tag{11.96}$$

With the exception of the second term, which is the result of fluid flow, i.e., of convection, this equation is identical to the one we will derive for time-dependent conduction of heat through a stationary body (see Chapter 13). An incompressible fluid with all quantities (mass, entropy, and momentum) flowing in only a single direction, displays the effects of the transport of entropy both due to conduction and to convection. Since there are no velocity gradients and no shear forces (requiring sideways flow of momentum), there are no viscous effects, and the momentum flux density (i.e., the pressure) must remain constant in the direction of flow. As a result, there is no reference to the mechanical processes to be found anymore in the resulting energy equation. This will not be the case for two-dimensional incompressible flow which we will study in the following section.

11.9 LESSONS OF CONTINUUM THERMODYNAMICS

Even though we have only had a very brief encounter with continuum thermodynamics up to this point, we can draw some important conclusions.

In view of our normal tendency to divide our description of the world into small, neat compartments, maybe the most important of the insights gained from continuum thermodynamics is that the classical field of thermodynamics and the subject of heat transfer form a natural unity. Despite all the claims of text books that heat transfer and thermodynamics do not mix, we do not have to artificially separate the two. Thermodynamics of uniform bodies can be presented as a theory of the dynamics of heat using the proper laws of balance of entropy, momentum, energy, etc., and associated constitutive relations; these same equations of balance are then used as the starting point for investigations of the flow of heat.

Problems in engineering and in the sciences are not solved if we put up high walls around each subject. Rather, if we accept the images inherent in continuum physics for the description of simpler examples as well, these walls are brought down. Introductory physics and thermodynamics would profit considerably from a careful look at what continuum processes have to tell us. Students who have grown up with this kind of mental picture will more easily venture into the exciting combined field of thermodynamics and heat transfer.

Continuum processes are clearly irreversible. While the quest for a description of reversible processes is understandable, and while theories of the dynamics of such processes can be built and applied successfully, the belief that reversibility requires equilibrium in the sense of static conditions has led classical thermodynamics into a tight corner out of which it can escape only if the lessons of continuum physics are learned. If you have followed the development of ideas in this book, you will have seen that everyday phenomena suggest an image of heat as the fundamental extensive thermal quantity leading directly to the equation of balance of entropy. Applying this law to continuum processes is therefore natural and straightforward, and its success tells us that self-imposed limitations in classical thermodynamics are unjustified and unnecessary.

The development of continuum physics in the 20th century should give us the courage to strengthen and renew our teaching of classical physics, to expose students of the sciences and engineering to the foundations of the classical fields, so that these foundations may be applied to the solution of current and future problems.

EXERCISES AND PROBLEMS

1. Consider the model of the life and migration of locusts (Section 11.1). Show that, on purely mathematical grounds, we cannot distinguish between production rate densities and source rate densities. What is their difference, then?
2. Create a uniform systems representation of the spatially continuous case of the law of balance of the locust model. Divide the one-dimensional space into a number of elements. Include migration on the ground and births and deaths. (a) Sketch the diagram of a system dynamics model. (b) Write the equation(s) for a single element of this pseudo-finite-element model. (c) Compare the equation(s) to the continuous case. Can the uniform model be recovered from the continuous case, or vice-versa? (d) In the uniform case, it appears to be impossible to distinguish between (conductive) flows and birth or death rates on purely mathematical grounds. Why? What is their difference, then?
3. Consider the locust model as in Equ.(11.10). (a) Write the equation for constant conductivity and no births and deaths. (b) What will the solution of this equation be for the time-independent (steady-state) case? What (and how many) boundary conditions are needed? How does the solution depend upon the particular boundary conditions you chose?
4. Consider the locust model as in Problem 3 but take a non-zero death rate as in Equ.(11.10); the death rate is assumed to be independent of time and space. What will the steady-state solution of this equation for constant conductivity be? What (and how many) boundary conditions are needed?
5. Add food as a new species to the one-dimensional locust model. The food resource cannot move, it can only be produced and destroyed. (a) Formulate the law of balance of food for the spatially and temporally continuous case. (b) Write constitutive relations for the production of food (example: logistic growth) and for destruction (consumption), and add these to the law of balance.
6. Show that the component form of the general equation of balance of momentum should be written as follows:

$$\frac{\partial}{\partial t}\left(\rho v_i\right)+\frac{\partial}{\partial x_j}\left(\rho v_i v_j + j_{pij}{}^{(c)}\right)=\sigma_{pi}$$

   Write all of the equations in fully expanded form.
7. Show that the law of balance of entropy in the form of Equ.(11.59) looks as if it represented the case of pure conductive transport of entropy. Does the law expressed by Equ.(11.59) exclude the phenomenon of convection? Can you explain the name *material derivative* given to the operator in Equ.(11.58)?
8. Write the law of balance of mass using the material derivative. Do the same for the simple case of pure one-dimensional transport of momentum.
9. In the purely one-dimensional case, gradients and divergences look the same. Explain their differences and write gradient (of a scalar function) and divergence (of a vector field) for a two-dimensional case.
10. Derive the general three-dimensional form of the substantial (material) derivative. Write the result both in coordinate-independent form and by using Cartesian coordinates.
11. Consider a flat car filled with water and travelling horizontally. Water flows out of the bottom through a hole. Determine the flux densities and the fluxes of momentum with respect

to a stationary control volume.

12. Perform a direct derivation of the balance of energy for purely one-dimensional convective and conductive flow of entropy as in Equ.(11.96). (*Hint:* Use a stationary control volume and compute convective and conductive currents of energy associated with entropy transfer only.)
13. Derive the complete expression for the rate of production of entropy for general three-dimensional flow of a Navier-Stokes-Fourier fluid.

CHAPTER 12

THERMODYNAMICS AND RADIATIVE TRANSFER

In this final chapter of Part III, thermal radiation will be studied from various perspectives that go beyond the uniform systems view taken in Chapter 7. The treatment offered here will not be a complete continuum model; rather, we will take a closer look at some aspects that make radiation unique among the heat transfer modes. Certain forms of distributions of radiation need careful consideration. First, we need to take a look at the angular distribution of radiation in space (Section 12.1), then the spatial distribution of absorption and emission (Section 12.2) will be dealt with. Finally, spectral distribution and polarization will be discussed in detail (Section 12.3 and Section 12.4). Applications of radiative transfer—essentially in the field of solar energy engineering—will be treated in Chapter 16.

12.1 RADIATIVE TRANSPORT OF HEAT

The most important point for us to understand about radiation is that we have to distinguish between the transport of entropy and energy through the radiation field, and absorption and emission of radiation by bodies (Section 12.2). The latter phenomenon is the result of the interaction of bodies and fields. Since the details of radiative transfer of entropy are at least as complicated as the transport of entropy by convection, we shall deal only with its most fundamental aspects.

12.1.1 The Flow of Entropy and Energy Through the Radiation Field

Entropy and energy are transported through space by electromagnetic radiation. Since visible light is the most obvious part of the spectrum of radiation, we shall often use the term *light* instead of the word *radiation*. As a first step, we will discuss the flow of entropy through the radiation field in the absence of bodies, examples of which are furnished by radiation in a cavity such as in Fig. 7.14, or in the space between the Sun and the Earth. Radiative transport is more complicated than conduction or convection in the sense that it is not sufficient to specify a radiative flux density vector of entropy (or energy) at every point of space. There is such a vector quantity which describes the net rate per unit area at which entropy is transported at a given point (Fig. 11.5). This net rate is, however, the result of entropy being carried by radiation in every direction of space at every point. Put differently, light may be traveling in any direction of space

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from a point and it may arrive at this point from any imaginable direction. Only if we manage to describe the flow of radiation in detail will the condition of the field be specified completely.

Distribution functions and intensity. To mathematically describe the radiation field, a *distribution function* is commonly introduced which is used to specify two fundamental properties of this system. First, radiation possesses a *density of entropy* and energy at every point in space and time. Second, at every point in space, radiation is traveling in different directions which cover at least a thin cone of finite solid angle, however small (Fig. 12.1). Rays of perfectly parallel light do not exist. Radiation may even be flowing in all directions of space in equal amounts, in which case the field is called *isotropic*. To capture this feature, we determine the *distribution of directions* of flow, i.e., the fraction of the density of entropy (or energy) which belongs to radiation moving in a cone pointing in a given direction (Fig. 12.1).

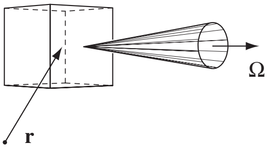

Figure 12.1: Radiation contained in a small volume about point **r** travels in all possible directions. A certain fraction of this radiation will be flowing in the direction within the solid angle shown in the figure. The flux density per unit solid angle is called the intensity of the radiation.

Both these properties, namely density and distribution of directions, are included in the distribution functions for entropy and energy (in the following, X will stand for either quantity). The function $f_X(t,\mathbf{r},\Omega)$ is said to represent the density of entropy or energy of radiation at time t and at point $\mathbf{r}$ traveling in a cone about the direction $\mathbf{\Omega}$ divided by the solid angle covered by the cone. The definition of this distribution function tells us that we obtain the density of quantity X by integrating the distribution over the complete sphere (solid angle 4π):

$$\rho_X(t,\mathbf{r}) = \int_{(4\pi)} f_X(t,\mathbf{r},\mathbf{\Omega})d\Omega \tag{12.1}$$

In the theory of heat transfer, we are interested in the rate of flow of entropy or energy in given directions. The entropy contained in the field is transported at the speed of light. In this respect, radiative transfer resembles convection where entropy stored is transported with the speed of the flowing medium. The same relation therefore holds between the density of entropy (or of energy) and the flux density in the case of radiation as well. In other words, the quantity

$$i_X(t,\mathbf{r},\mathbf{\Omega}) = c\, f_X(t,\mathbf{r},\mathbf{\Omega}) \tag{12.2}$$

represents the flux density of quantity x at point $\mathbf{r}$ of radiation traveling within the cone of Fig. 12.1 which is pointing in direction $\mathbf{\Omega}$ divided by the solid angle of the cone. This quantity is called the *intensity of radiation*, measured either in terms of entropy or of energy (the units are W/(K·m^2·sr) and W/(m^2·sr), respectively, where sr is the unit of the solid angle). To be specific, for the measurement of the intensity at point $\mathbf{r}$ we imagine a small area perpendicular to the direction $\mathbf{\Omega}$. We compute the flux of the radiation flowing within a narrow cone pointing in the direction of the vector $\mathbf{\Omega}$ and divide this quantity by the surface area to obtain the flux density of the fraction of radiation under consideration. Finally, we divide the result by the solid angle of the cone. Note that the condition of the radiation field is described completely in terms of either the distribution functions or the intensities.

Now, using the intensity, we may express the density of quantity X of the radiation field. By combining Equations (12.1) and (12.2) we obtain:

$$\rho_X(t,\mathbf{r}) = \frac{1}{c}\int_{(4\pi)} i_X(t,\mathbf{r},\mathbf{\Omega})d\Omega \tag{12.3}$$

The intensity of blackbody radiation. The special case of isotropic radiation is of particular importance for us. Just consider the radiation contained in the cavity of Fig. 7.14. Black body radiation does not depend upon the properties of the cavity walls. The only parameter influencing this type of radiation is the temperature T. Since T is the same everywhere, the entropy arriving from different directions in the cavity must be the same. In other words, the intensity is independent of direction. Therefore, the integral in Equ.(12.3) may be evaluated easily. The solid angle of the complete sphere is 4π. For this reason, we obtain the following expression for the *density of isotropic radiation:*

$$\rho_X = \frac{4\pi}{c} i_X \tag{12.4}$$

We may now express the intensities of *blackbody radiation* in terms of the densities of entropy and of energy which have been derived in Section 5.4:

$$i_{Sb} = \frac{c}{3\pi} aT^3 \tag{12.5}$$

and

$$i_{Eb} = \frac{c}{4\pi} aT^4 \tag{12.6}$$

In these relations, the index b refers to blackbody. These equations support the claim about the temperature dependence of entropy and energy fluxes in radiation made in Section 7.4.1.

The flux density. One of the problems encountered in radiative heat transfer calculations is the question of how much entropy and energy penetrate a given surface in a certain amount of time. Related to this problem is the computation of one-sided fluxes, i.e., the rates at which entropy or energy flow from one side of a surface to the other. Consider a part of an imaginary or real surface of size ΔA in a radiation field, such as in Fig. 12.2. The orientation of the surface is determined by the unit vector **n** normal to the surface. The rate at which entropy or energy flow through this area is equal to the corresponding flux through an imaginary sphere of radius r centered on it. Consider the portion of the radiation which travels through the surface within a narrow cone in the direction of the vector Ω. The latter is tilted at an angle θ with respect to **n**. The cone cuts a circular area out of the imaginary sphere, and the radiation flux I_X through the cone is proportional to this area; furthermore, it is inversely proportional to the square of the distance from ΔA. In other words, the flux is proportional to the solid angle of the cone. Finally, it is proportional to the projection of ΔA perpendicular to the direction of the flow of radiation, which is $\Delta A \cos(\theta)$. The flux density of radiation contained within the cone is found by dividing the flux by ΔA. The total flux density is finally obtained by integrating over the entire sphere, i.e., over the complete solid angle. Combining all of this information, we can express the flux density of quantity x as follows:

$$j_X = \int_{(4\pi)} i_X \cos(\theta) d\Omega \tag{12.7}$$

This quantity is not a vector, as a proper flux density would be. Rather, it is the component of the flux density vector in the direction of **n**. However, this point does not

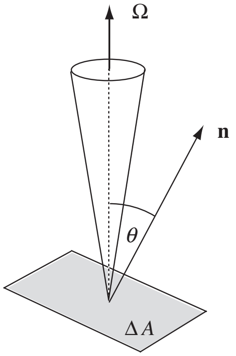

Figure 12.2: Part of an imaginary (or real) surface is penetrated by radiation. The vector **n** determines the orientation of the surface. Consider entropy flowing within a cone centered on the direction of the vector Ω (which represents part of the total entropy flux through the surface ΔA). The flux through the surface due to radiation in the cone depends upon the orientation of the cone with respect to the surface. The problem is to compute either the total flux with respect to ΔA, or the one-sided or hemispherical flux.

have to concern us here. Note that the fluxes given by Equ.(12.7) are zero for isotropic radiation: equal amounts of entropy or energy flow from one side to the other, and back again. This condition is satisfied, for example, by blackbody radiation inside a cavity, or by radiation in an extended body where the radiation and body have the same temperature.

The flux density of radiation flowing from one side of a surface to the other is called the *hemispherical flux density* j_X'. It is of practical importance since it represents, for example, the entropy or the energy radiated per time and per unit area by the surface of a hot body (Section 7.4). The hemispherical flux density is obtained by integrating the expression in Equ.(12.7) over a hemisphere instead of over the entire sphere. For *isotropic* radiation the result is particularly simple:

$$j_X' = \pi i_X \tag{12.8}$$

Details of the derivation of this equation are provided below in Equ.(12.13). The result for the hemispherical flux density of entropy and energy of *blackbody* radiation is of special interest:

$$j_{Sb}' = \frac{4}{3}\sigma T^3 \tag{12.9}$$

and

$$j_{Eb}' = \sigma T^4 \tag{12.10}$$

where

$$\sigma = \frac{1}{4} c a \tag{12.11}$$

Here, σ is called the *Stefan-Boltzmann constant*. It is a combination of the radiation constant a and the speed of light. It has a value of $\sigma = 5.67 \cdot 10^{-8}\ \mathrm{W \cdot m^{-2} \cdot K^{-4}}$. It was used in Chapter 7 to calculate radiative entropy and energy transfer.

Hemispherical flux density for isotropic radiation. To obtain the rate of transfer of entropy or energy flowing through a surface towards one side, we need to evaluate Equ.(12.7) for the flux density for a hemisphere. As before the variable *X* stands for either entropy or energy of radiation:

$$j_X' = \int_{(2\pi)} i_X \cos(\theta) d\Omega \tag{12.12}$$

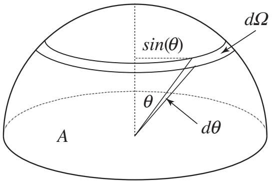

Figure 12.3: Radiation flows isotropically from the lower toward the upper side of surface *A*. The total entropy or energy carried through the surface from one side to the other per unit time is called the hemispherical flux density.

The intensity has to be integrated over one side of the area *A* (Fig. 12.3). Remember that we are dealing with isotropic radiation. This means that the quantities appearing in the integral are independent of the longitudinal angle. We can divide the surface of the hemisphere into small circular rings whose areas are

$$d\Omega = 2\pi \sin(\theta) d\theta$$

The hemisphere has a radius of unity. Therefore, the area of a ring translates directly into the solid angle associated with it. Now we can perform the integration indicated in Equ.(12.12), which leads to:

$$j_X' = \int_0^{\pi/2} i_X \cos(\theta) 2\pi \sin(\theta) d\theta = \pi i_X \int_0^{\pi/2} \sin(2\theta) d\theta = \pi i_X \tag{12.13}$$

This result holds for isotropic radiation in general. j_X' represents the amount of quantity X transferred from one side of an area A to the other, per time and per unit area. It includes all the radiation traveling in all directions seen from one side of the surface A. This is the result presented above in Equ.(12.8).

12.1.2 The Radiation Shape Factor

The formulas derived for the fluxes of entropy or energy exchanged between surfaces hold only for the special case where all the radiation emitted by one of the bodies is intercepted by the other, as with the small piece of matter inside the cavity in Fig. 7.14. In many practical cases, the geometrical arrangements are more complex. The particular geometry is taken into account via a *radiation shape factor* (which also is called the *view factor* or the *configuration factor*).

As a more general case, consider two black surfaces as in Fig. 12.4. The orientation of each of the surfaces is given by a unit normal vector. Let us calculate the flux of energy emanating from surface 1 which is intercepted by a small part of the second area. This quantity is the intensity of radiation emerging from A_1, multiplied by the direction cosine of angle θ_1, and by the solid angle subtended by the small area on surface 2. Finally we have to multiply this expression by the area on surface 1 from which the radiation originates. The flux of energy flowing from surface 1 to surface 2 is then

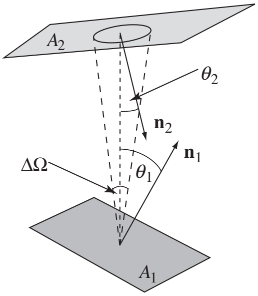

Figure 12.4: Radiative exchange of heat between two black surfaces. Their sizes and orientations are arbitrary. The figure shows a part of the radiation flowing from surface 1 toward surface 2.

$$I_{E12} = \int_{A_1} \int_{\Omega} i_{Eb} \cos(\theta_1) d\Omega \, dA_1 \tag{12.14}$$

The solid angle subtended by a small area on surface 2 may be expressed in terms of the distance r between the surfaces and the projection of this area perpendicular to r. Using the direction θ_2, Equ.(12.14) becomes

$$I_{E12} = \int_{A_1} \int_{A_2} i_{Eb} \cos(\theta_1) \frac{\cos(\theta_2) dA_2}{r^2} dA_1 \tag{12.15}$$

If we now invoke the law of Stefan and Boltzmann, the final result is

$$I_{E12} = \frac{\sigma T_1^4}{\pi} \int_{A_1} \int_{A_2} \frac{\cos(\theta_1)\cos(\theta_2)}{r^2} dA_2 \, dA_1 \tag{12.16}$$

The same kind of expression emerges for the flux of radiation flowing from surface 2 to A_1, with the temperature T_2 substituted for T_1. The net flux therefore must be

$$I_{E,net} = \frac{\sigma}{\pi}\left(T_1^4 - T_2^4\right) \int_{A_1} \int_{A_2} \frac{\cos(\theta_1)\cos(\theta_2)}{r^2} dA_2 \, dA_1 \tag{12.17}$$

It is customary to write this in an abbreviated form which resembles the original expression for the law of Stefan and Boltzmann:

$$I_{E,net} = \sigma A_1 F_{12}\left(T_1^4 - T_2^4\right) \tag{12.18}$$

Therefore, the *radiation shape factor* F_{12} is related to the surfaces exchanging radiation by

$$A_1 F_{12} = \frac{1}{\pi} \int_{A_1} \int_{A_2} \frac{\cos(\theta_1)\cos(\theta_2)}{r^2} dA_2\, dA_1 \tag{12.19}$$

Note that we could have started by considering the radiation from surface 2. We would have obtained the same result, only with the surface area A_1 replaced by A_2. Therefore, F_{21} is related to F_{12} by

$$A_1 F_{12} = A_2 F_{21} \tag{12.20}$$

In practice, the computation of the integral may only be possible using numerical methods. Moreover, the result of Equ.(12.19) is not general. First of all, we have considered only two surfaces exchanging heat; second, the surfaces have been assumed to be black. Relaxing either of these conditions introduces additional complexities.[1]

12.2 ABSORPTION, EMISSION, AND KIRCHHOFF'S LAW

So far, we have discussed the flow of entropy through the radiation field only in the absence of bodies. Now we shall consider the interaction of a body with a radiation field in the space which is occupied by both systems.[2] In general, a body is bounded while the field associated with it may extend beyond the space filled by matter, in which case radiation penetrates the surface of a material body (Fig. 12.5).

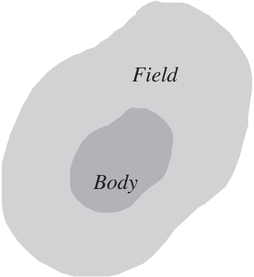

Figure 12.5: For a bounded body interacting with a radiation field, the field may extend beyond the volume occupied by the body.

12.2.1 Interaction of matter and radiation

Matter emits light, and it absorbs light. It may also scatter radiation. *Emission*, *absorption*, and *scattering* are the processes which make up the interaction of bodies with radiation. From the viewpoint of a body, emission and absorption are volumetric processes. In other words, light is emitted and absorbed by every part of a body. Entropy is not transported through matter; rather it appears in, or disappears from, every arbitrarily small part. Entropy appearing in a body disappears in the radiation field, and vice-versa. Obviously, this type of transport is comparable to the transport of momentum from fields to bodies due to their interaction. This is not to say that entropy does not flow through the space occupied by a body. However, if this is the case, entropy is transported through the radiation field. While radiation is created or destroyed in the processes of emission and absorption, scattering changes the direction of a ray of light without absorbing it. Even though this process may be important in some cases (just think of the scattering of light in the Earth's atmosphere), we shall neglect it in the following discussion. Still, one point deserves to be mentioned: while absorption

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1. For more details see Siegel and Howell (1992), Chapter 6.
2. Here, we can only touch upon this subject. If you wish to know more about it, you should read the book by Max Planck: *The Theory of Heat Radiation* (1906), which is still one of the best accounts of the physics of these phenomena. A modern and detailed text on the subject is *Thermal Radiation Heat Transfer* by Siegel and Howell (1992).

and emission depend on the frequency of radiation, this influence is particularly pronounced in scattering. In general, the magnitude of scattering increases strongly with increasing frequency of the light. This fact explains the blue color of the sky. Thus, we need to take into account the spectral dependence of the quantities introduced so far. However, we shall leave this point out of consideration for the moment and return to it in Section 16.1.2.

12.2.2 Processes at surfaces

Radiation which travels through a medium undergoes the three types of interaction mentioned before. When a ray of light reaches the surface of a body, however, we must deal with additional processes, namely reflection and refraction at the surface, and transmission into the medium adjacent to the body. These phenomena are known from optics, and they satisfy the laws of propagation of electromagnetic radiation at interfaces. Again, we shall not deal with these laws in any depth. Nevertheless, we need to know a few facts about the processes occurring at interfaces (see Fig. 12.6). In general, a surface separating two media will reflect at least part of the light incident upon it. The fraction of light reflected is called the *reflectivity*. The reflection may either be *specular*, in which case we shall call the surface smooth; or *diffuse*, which is the case for rough surfaces. The reflectivity usually depends on the angle of incidence of the ray of light, and on the wavelength. Also, a surface may be smooth for radiation of a particular frequency, and rough for light of another wavelength. If the reflection is specular and complete, we call the surface a *mirror*; if the reflection is complete and totally diffuse, the surface is called *white*. The opposite of a white surface is a *black* one, with zero reflectivity. The fraction of light incident on a surface and absorbed by the second body is called the *absorptivity*. By definition, the absorptivity of a black body is equal to 1. Black surfaces do not really exist in nature; for example, a smooth surface separating two optically different media cannot transmit all radiation incident upon it. In particular, if the speed of propagation of light is different in the bodies touching each other, the reflectivity cannot be zero. In general, therefore, a black surface should be rough, the body admitting the light should be thick enough for the radiation not to emerge from the other side, and it should not scatter radiation; otherwise the light transmitted would flow back towards the first body. With a smooth interface, the optical properties of the media must be the same for radiation to be transmitted completely.

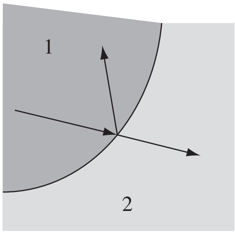

Figure 12.6: Surface phenomena involving radiation occur wherever different bodies touch. A "body" may also be vacuum.

12.2.3 Sources and sinks of radiation

Let us now turn to a more formal discussion of the interaction of matter and radiation. If we disregard scattering, the interaction is described using the source rates of entropy and energy which were introduced in the laws of balance in Equations (7.5) and (7.6). These determine the net rate at which an entire body exchanges entropy or energy with the field. If conditions inside a body vary from point to point, we have to introduce the *density of the source rate*, or simply, the *source density* of entropy or energy. These quantities have the units $W/(K \cdot m^3)$ and W/m^3, respectively. The source rates are obtained for a body by integrating the densities over its volume $\mathcal{V}$:

$$\Sigma_x = \int_{\mathcal{V}} \sigma_x \, dV \tag{12.21}$$

Again, *x* stand for entropy or energy. These densities play the same role as some quantities introduced previously, such as mass and entropy densities, the density of entropy production, the distribution function introduced above, or flux densities and the intensity of radiation. They all describe the spatial distribution of physical quantities, a feature we cannot do without in a continuum.

Physically, the source rate or its density are the result of emission and absorption of radiation by matter. It is customary to introduce *emission and absorption coefficients of energy* to describe the interaction of bodies and fields in more detail. These coefficients incorporate information concerning the distribution of directions of radiation. At every point inside a body, matter may emit radiation in any direction, and radiation which is absorbed may stem from rays traveling in different directions. The *emission coefficient* ε_E is defined as the rate of emission of energy per volume and per solid angle. In other words, the expression

$$\sigma_E^- = \int_{(4\pi)} \varepsilon_E(\Omega) d\Omega \tag{12.22}$$

represents the *density of the rate of emission* of energy. Absorption is introduced in terms of a coefficient α which plays a role comparable to ε. It is the rate at which energy is absorbed from the field per volume and per solid angle. The radiation absorbed depends on the intensity of radiation present in the field; in fact, for a short distance in the direction of a ray, the absorption density is proportional to the intensity. For this reason, one defines the *absorption coefficient* κ_E, which when multiplied by the intensity, yields the density of the rate of absorption per solid angle:

$$\alpha_E(\Omega) = \kappa_E i_E(\Omega) \tag{12.23}$$

The absorption coefficient κ_E has units 1/m. It describes the fraction of energy absorbed by the body from the field over a small distance, divided by this distance. Obviously, the *density of the rate of absorption* of energy is obtained if we integrate α_E over the solid angle:

$$\sigma_E^+ = \int_{(4\pi)} \kappa_E i_E(\Omega) d\Omega \tag{12.24}$$

Armed with these quantities we can finally express the source density of radiation in terms of emission and absorption coefficients. With

$$\sigma_E = \sigma_E^+ - \sigma_E^- \tag{12.25}$$

we obtain for a body contained in volume $\mathcal{V}$:

$$\Sigma_E = \int_{\mathcal{V}} \int_{(4\pi)} \left(\kappa_E i_E - \varepsilon_E \right) d\Omega \, dV \tag{12.26}$$

Remember that all of these quantities have been defined with respect to the body, and not with respect to the radiation field. The signs appearing in Equations (12.25) and (12.26) reflect this assumption. Since both the rate of absorption and the rate of emission are taken to be positive quantities, emission leads to a loss of entropy in a body, while the body will gain entropy through absorption. The results just derived will now be used in formulating an important relation in radiative transfer.

12.2.4 Kirchhoff's Law

The foregoing discussion involves the definition of quantities which are used in a continuum theory. Now, we will motivate an important relation of the theory of radiative transfer—a simple relationship between the coefficients of absorption and of emission called *Kirchhoff's law*.

To appreciate this law, we must first figure out the condition of the radiation field generated by a body. Initially, we shall assume this body to be very large and isotropic. It is supposed to be enclosed by an adiabatic wall. If conditions are not uniform at the beginning, they will soon be, because of conduction and radiative exchange of heat. In a fluid, differences in pressure and density will quickly smooth out. After some time, we will have a uniform isotropic body in steady state. In the end, the only free parameter describing the state of a body of given composition will be the temperature. Under these circumstances, the radiation field will be isotropic and uniform as well. First of all, the intensity of radiation must be isotropic and the same for points of the body far enough from the surface. These points are not influenced by the wall, and there is no reason why conditions should be different at different locations. For every bundle of rays propagating through a small surface inside the body within a small solid angle, there is light flowing with equal intensity in the opposite direction converging toward the imaginary surface. In other words, the intensity must be isotropic and uniform and may depend only upon the temperature and the composition of the medium.

Actually, the state of the radiation field cannot be any different near the surface of the body under consideration. A ray flowing from the surface toward points inside the medium must have the same intensity as a ray traveling in exactly the opposite direction from interior points towards the wall. If this were not the case, we would end up with a net transport of entropy and energy in a particular direction. This would disturb the uniform and steady conditions which have already been reached. As a consequence, the body whose field we are investigating does not have to be large at all. Indeed, it may be arbitrarily small and of any shape, and the radiation field will be uniform and isotropic throughout.

We may now consider small bodies of differing composition in contact with each other. Each body shall be taken to be uniform and isotropic. If they have the same temperature, entropy will flow from one to the other only by means of radiation. Assume the speed of propagation of light to be same in all of them, and let each ray be transmitted directly through the surfaces. (Actually, these conditions can be relaxed, and the problem of the speed of light can be taken care of;[3] however, we shall not discuss this point here). The same kind of reasoning tells us that the intensity of radiation must be the same in two adjacent media. A ray traveling in a particular direction from one of the bodies will be transmitted by the wall separating the different regions of space. It should not matter to the second body where the ray comes from. Again, its intensity must be the same as that of a ray propagating in the opposite direction. Therefore, we conclude that the intensity of radiation found in a large body made up of small regions of different materials cannot depend on its composition. All in all, only the temperature may influence the state of the radiation field. This conclusion is very important: it means that *if we know the intensity as a function of temperature for one medium, we know it for all media in the system.*

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[3] M. Planck (1906, 1921).

Finally, consider one of the parts of the body to be a cavity surrounded by matter. For the reasons just listed, the radiation inside this cavity must be the same as that found inside the volume occupied by matter. Remember that for simplicity the optical properties of all media, and therefore also of empty space, have been assumed to be the same. Since we know the field in the cavity to be that of *blackbody radiation*, the same must be true for the field of the entire uniform and isotropic body. In other words, the intensity of radiation is given by Equations (12.5) and (12.6).

Now we are ready to state *Kirchhoff's law*. Under stationary conditions in a body of the type discussed, the net source rate of energy must be zero. If this were not so, the body would heat up and cool down at different points, contrary to our assumption. Therefore, the expression in Equ.(12.26) must vanish. Since this is true for bodies of any size and shape, the integrand, which itself is an integral over solid angle, is equal to zero at every point inside the body. Finally, since the radiation field is isotropic, we find that

$$i_{Eb}(T) = \frac{\varepsilon_E}{\kappa_E} \tag{12.27}$$

In other words, while the coefficients of absorption and of emission depend upon the composition of bodies (and on temperature), their ratio is a universal function of temperature only. If one of the coefficients is known, the other may be calculated from Kirchhoff's law. Note that Equ.(12.27) holds at every point in a body.

We have found Kirchhoff's relation by considering uniform conditions with the radiation field having the same temperature as matter. At first sight it may appear as if this is true only if the radiation has blackbody characteristics. However, the coefficients of absorption and emission depend only on the properties of matter, not on those of the field. Their ratio must therefore be independent of the actual intensity of radiation. If the radiation inside a body is not black, the net source rates of entropy and energy simply do not vanish. Indeed, if *i* is the intensity of radiation in a volume occupied by matter, the source rate of energy turns out to be

$$\Sigma_E = \int_{\mathcal{V}} \int_{(4\pi)} \kappa_E \left(i_E - i_{Eb} \right) d\Omega \, dV \tag{12.28}$$

This result, which is a consequence of Kirchhoff's law, has been derived from the expression in Equ.(12.26).

Remember that, in deriving Equ.(12.28), scattering has not been considered. Under conditions found here on Earth, its influence may often be left out of consideration;[4] in astrophysical applications, however, it may be much more important.[5] Also, the phenomenon of *stimulated emission* of radiation has been ignored. The emission coefficient introduced above is that of *spontaneous emission*. Stimulated emission results from radiation present in a medium, and its effect is proportional to the intensity of light passing through the medium. Since this is true for absorption as well, stimulated emission tends to reduce the value of the absorption coefficient. We may still

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[4] However, this certainly cannot be done if the flow of solar radiation through the Earth's atmosphere is to be calculated (Chapter 16).

[5] S. Chandrasekhar (1960).

work with Equ.(12.26), replacing the absorption coefficient by a somewhat different expression.[6]

12.2.5 Radiative Transfer Through a Medium with a Temperature Gradient

How does the interior of the moon cool, or how is entropy transported through a star? It might surprise you that in both of these cases radiative transfer plays an important role, even though the bodies appear to be virtually opaque. Still, if transport by means of conduction or convection is not efficient enough, then entropy must flow through the radiation field inside the bodies while it is continually absorbed and emitted.

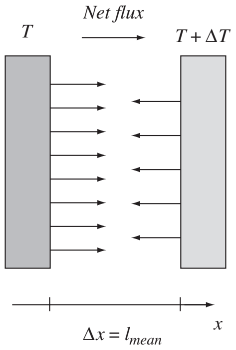

Figure 12.7: Radiative transfer through a planar medium having a temperature gradient. If the two surfaces have different temperatures, there results a net flow of entropy and energy through the field from the hotter to the cooler surface.

Consider one-dimensional heat flow through a planar slab of matter as in Figure 34. Consider two surfaces facing each other at a distance equal to the mean distance between consecutive events of emission and absorption of radiation, which is sometimes called the *mean free path* of the radiation. We model absorption and emission of entropy inside the body by the absorption and emission of these surfaces. Each surface radiates entropy and energy toward the other, according to its temperature. If they are at the same temperature, there is no net flux of entropy or energy between them. However, if one of them has a lower temperature than the other, a net flux results. If we assume conditions where the radiation field is that of a black body, the net current density in the direction of decreasing temperature can be approximated by the temperature gradient. The expression

$$j_E = \sigma\left[\left(T + \Delta T\right)^4 - T^4\right] \approx \sigma 4 T^3 \Delta T$$

can be written

$$j_E = -4\sigma l_{mean} T^3 \frac{dT}{dx} \tag{12.29}$$

In this form, the transfer of entropy looks very similar to that of conduction: the flux of entropy or energy is proportional to the temperature gradient of the material. The factor multiplying the gradient can be interpreted as a kind of thermal conductivity (with respect to energy):

$$k_{E,rad} = 4\sigma l_{mean} T^3 \tag{12.30}$$

Because of this, radiative transfer of heat through matter with a temperature gradient is often called *diffusion of radiation*. Its efficiency depends upon the properties of the body expressed by the mean free path. Particularly in astronomy, the mean free path is replaced by the *opacity*, which is defined as the fraction of radiation absorbed by a slab of matter (Problem 6).

Note that we have introduced the flux density of entropy here as in conduction and convection, even though entropy is transported radiatively. However, as you can tell from this discussion, we can easily interpret the net result of this transport in terms of

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[6] Zel'dovich, Raizer (1966), vol. I, p. 118.

the flow of entropy *through* the body which is permeated by the radiation field. In fact, we do not even consider the field anymore in our description.

12.3 THE SPECTRAL DISTRIBUTION OF RADIATION

In the preceding sections we have neglected an important feature of radiation, namely its spectral dependence. Just about all the quantities introduced so far depend on the frequency of the light transporting entropy and energy. For example, in the forms stated above, Kirchhoff's law cannot generally hold with a single value of absorptivity and emissivity independent of frequency. With the model of gray surfaces we were not able to account for the temperatures attained by bodies in the light of the Sun (remember Example 7.12). The difficulty can be resolved only if we accept that absorption and emission depend upon the frequencies of the light absorbed or emitted.

Therefore, we need to know the spectral distribution of radiation. The problem of how to obtain it from first principles was solved for blackbody radiation by Max Planck.[7] He was able to calculate the distribution of energy and entropy in the *normal spectrum*, i.e., in the spectrum of blackbody radiation. Moreover, he argued how, on the basis of Wien's displacement law, the results can be extended and the temperature of rays of monochromatic radiation can be derived. Since we must often deal with nonblackbody radiation, this is an important result, which we are going to use in calculating the entropy of solar radiation here on Earth (Chapter 16).

In the following paragraphs we will first explain how to introduce the spectral dependence of radiative quantities. Then, Kirchhoff's law will be stated in its general form, and Planck's result for the distribution of energy and entropy in the normal spectrum will be presented. Finally, the reasoning which leads to a generalization of the results to nonequilibrium radiation will be outlined. As before, a number of simplifications will be made. The influence of the speed of light in different media will not be considered; and we will neglect scattering of radiation until we treat the special case of solar radiation in the Earth's atmosphere.

12.3.1 Dependence of Radiative Quantities Upon Frequency

The fundamental terms used in the description of the radiation field are the distribution functions f_X and the intensities i_X. Obviously, these must depend upon the frequency of a ray of light. To capture this property of radiation, we introduce the *spectral distribution functions* $f_{X\nu}$ and the *spectral intensities* $i_{X\nu}$. (As before, X stands for both entropy and energy.) Again these represent some sort of density, this time with respect to frequency. If we integrate these densities over the entire range of frequencies of the electromagnetic spectrum, we recover the overall quantities introduced before:

$$f_X(t,\mathbf{r},\mathbf{\Omega}) = \int_0^\infty f_{X\nu}(t,\mathbf{r},\mathbf{\Omega},\nu)\,d\nu \tag{12.31}$$

and

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[7] M. Planck: *The Theory of Heat Radiation* (1906).

$$i_X(t,\mathbf{r},\mathbf{\Omega}) = \int_0^\infty i_{X\nu}(t,\mathbf{r},\mathbf{\Omega},\nu)\,d\nu \qquad (12.32)$$

The volume densities of entropy and energy of the radiation field have therefore a spectral dependence as well. The *spectral density of entropy* and the *spectral density of energy* of the field are denoted by $\rho_{S\nu}$ and $\rho_{E\nu}$, respectively. They are obtained in terms of the spectral distribution function or the spectral intensity if we replace the original quantities in Equ.(12.3) by the spectral ones. As a consequence, the densities are computed by integration of the spectral functions over frequency:

$$\rho_X = \int_0^\infty \rho_{X\nu}\,d\nu \qquad (12.33)$$

In fact, if appropriate, all the quantities introduced in the previous paragraphs relate to their spectral counterparts in just this way. There is one exception to the rule, namely the absorption coefficient κ_E defined by Equ.(12.23). The spectral coefficient $\kappa_{E\nu}$ exists, but it cannot be integrated by itself to give the original quantity. Rather, we have to replace Equ.(12.23) by

$$\alpha_{E\nu}(\Omega) = \kappa_{E\nu} i_{E\nu}(\Omega) \qquad (12.34)$$

This equation must be integrated over the entire range of frequencies to yield the expression found in Equ.(12.23).

The relation between the density and the intensity of radiation derived for isotropic flow carries over to the spectral quantities. For entropy and energy, we have

$$\begin{aligned} \rho_{S\nu} &= \frac{4\pi}{c} i_{S\nu} \\ \rho_{E\nu} &= \frac{4\pi}{c} i_{E\nu} \end{aligned} \qquad (12.35)$$

Often, the spectral densities and intensities are written with respect to wavelength λ instead of frequency. Since the total intensity i_X must be the same if calculated from the spectral intensity with respect to frequency or from the spectral quantity $i_{X\lambda}$, we get

$$i_X = \int_\nu i_{X\nu}\,d\nu = \int_\lambda i_{X\lambda}\,d\lambda = \int_\nu i_{X\lambda}\frac{c}{\nu^2}\,d\nu$$

The last step is a consequence of the relation between the speed of propagation of radiation, its frequency, and its wavelength, i.e., $c = \nu\lambda$. Comparing the first and the third integrals we obtain

$$i_{x\lambda} = \frac{\nu^2}{c} i_{x\nu} = \frac{c}{\lambda^2} i_{x\nu} \qquad (12.36)$$

for the law of transformation from frequency-dependent quantities to those referring to wavelength.

The spectrum of solar radiation. An example of the spectral distribution of radiation is provided by the solar spectrum. The Sun radiates mostly in the visible part but its light also contains important contributions from ultraviolet and infrared radiation. Fig. 12.8 shows the intensity of solar radiation outside the Earth's atmosphere, which should correspond to the light produced in the photosphere of the Sun. Note that according to Equ.(12.36), the peak of the distribution is not at the same wavelength if the spectral values are measured with respect to the frequency of radiation.

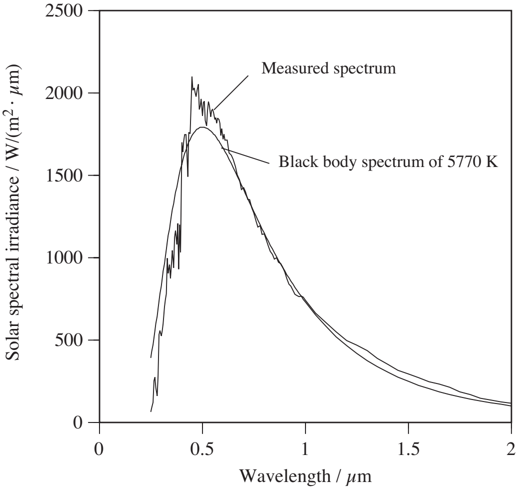

Figure 12.8: Spectral intensity (with respect to wave-length) of solar radiation. The spectrum is similar to that of radiation from a black body at a temperature of about 5800 K (see Fig. 12.10). The integral of this quantity taken over wavelength must yield the total intensity, which in this case, is $2.01 \cdot 10^7$ W/(m$^2 \cdot$ m $\cdot$ sr). Data represent the World Radiation Center (WRC) spectrum and were taken from Iqbal (1983).

12.3.2 Kirchhoff's Law

We can more generally express the source rate of energy which was first calculated in Equ.(12.26). The quantities relating to the absorption and emission of radiation have to be integrated over frequency, solid angle, and volume:

$$\Sigma_E = \int_0^\infty \int_V \int_{(4\pi)} \left(\kappa_{E\nu} i_{E\nu} - \varepsilon_{E\nu}\right) d\Omega \, dV \, d\nu \tag{12.37}$$

This leads to an important result, *Kirchhoff's law*, which can now be stated in its general form:

$$i_{E\nu b}(T,\nu) = \frac{\varepsilon_{E\nu}}{\kappa_{E\nu}} \tag{12.38}$$

Kirchhoff's law results from Equ.(12.37) if we accept that the source rate must vanish separately for each frequency in a uniform body under steady-state conditions for which the radiation field is that of blackbody radiation. (Therefore, the blackbody intensity appears in Equ.(12.38).) If the source rate did not vanish for every color of light separately, the spectral distribution of radiation would change due to selective absorption and emission. This contradicts our assumption that the spectral intensity of the radiation field should not change with time. Remember that the intensity of blackbody radiation must be independent of the medium; the reasons are the same as those given in Section 12.2. Therefore, while the spectral coefficients of absorption and of emission in general depend upon the material absorbing and emitting radiation, their ratio is a unique function of temperature.

12.3.3 Wien's Displacement Law

Recognizing that radiation quantities depend upon frequency raises the question of the form of the spectral distribution of blackbody radiation. A first step toward solving this problem can be made by deriving Wien's displacement law. The idea is to calculate the change of the frequency distribution of radiation which results from reversible adiabatic compression or expansion of radiation contained in a cavity with perfectly reflecting walls, and with no trace of an absorbing or emitting medium inside (see Fig. 12.9). It is important to recognize that the following derivation holds for radiation of any spectral distribution, not just for blackbody radiation;[8] however, we will assume the radiation in the cavity to be isotropic.

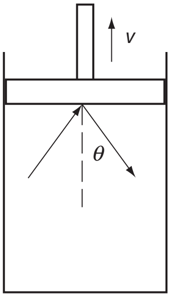

Figure 12.9: Radiation of an arbitrary spectral distribution is expanded adiabatically inside a cavity having reflecting walls and a piston. The radiation striking the moving piston changes its frequency as a result of the Doppler effect.

Let us now calculate the rate of change of the spectral energy of the radiation inside the cavity as the piston is pulled or pushed. The spectral energy is the product of the instantaneous volume of the cavity and the spectral energy density. In other words, we wish to calculate the quantity

$$\frac{d}{dt}\left(V\rho_{E\nu}\right)$$

The frequency distribution will change as a result of radiation hitting the moving piston, i.e., as a consequence of the Doppler effect. Let us consider a particular frequency ν. If radiation of that frequency bounces off the piston, it will have a different color. This means that the spectral energy at frequency ν will be reduced by just the amount of energy contained in the radiation flowing toward the piston. With isotropic light, the spectral energy flux striking the piston of surface area A must be

$$j_{E\nu}{}^{'-} = \pi A i_{E\nu}$$

which is the rate at which the spectral energy at frequency ν is depleted. The second effect will add radiation of frequency ν to the spectrum. If light of a frequency ν_1, which is larger than ν, strikes the receding mirror, it will become radiation of frequency ν. The formulas for the Doppler effect let us calculate the relation which must hold between the rays of the two different frequencies ν and ν_1:[9]

$$\nu_1 = \nu\left(1 + \frac{2v\cos\theta}{c}\right) \tag{12.39}$$

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[8] If the cavity contains absorbing and emitting matter, the radiation within it would become blackbody radiation. This is why the walls must be perfectly reflecting.

[9] For relative speeds u of observer and light source which are small compared to the speed of light, the relation should be

$$\nu = \nu_1\left(1 - \frac{u}{c}\right)$$

which reduces to Equ.(12.39); ν is the frequency of the reflected radiation while ν_1 is that of the original light. Note that the light reflected from the receding mirror seems to come from a source which recedes at twice the speed of the mirror. Naturally, a ray parallel to the mirror will not experience any Doppler shift.

θ is the angle between the direction of a ray and the normal to the surface of the piston, and v is the speed of the piston. The spectral intensity of the light which will add to the rays of frequency ν is $i_{E\nu 1}$. This quantity can be approximated by $i_{E\nu}$ as follows:

$$i_{E\nu 1} = i_{E\nu} + \left(\nu_1 - \nu\right)\frac{\partial i_{E\nu}}{\partial \nu} + \ldots$$

If we calculate the difference between frequencies according to the Doppler effect and neglect higher order terms in the expansion, we obtain

$$i_{E\nu 1} = i_{E\nu} + \nu \frac{2v\cos\theta}{c}\frac{\partial i_{E\nu}}{\partial \nu}$$

for the intensity of the radiation which will be changed into light of the desired frequency. We again have to integrate this quantity over the hemisphere to get the energy flux responsible for increasing the spectral energy at frequency ν:

$$j_{E\nu}{}'^{+} = \pi A i_{E\nu} + \pi\nu \frac{4}{3c}\frac{\partial i_{E\nu}}{\partial \nu}\dot{V}$$

Note that the product of the speed of the piston and its surface area is equal to the rate of change of the volume of the cavity. Now, the balance of energy for frequency ν is given by

$$\frac{d}{dt}\left(V\rho_{E\nu}\right) = j_{E\nu}{}'^{+} - j_{E\nu}{}'^{-}$$

which, according to Equ.(12.35)$_2$, is equivalent to

$$V\dot{\rho}_{E\nu} + \rho_{E\nu}\dot{V} = \frac{1}{3}\nu\frac{\partial \rho_{E\nu}}{\partial \nu}\dot{V}$$

This finally yields the differential equation

$$\dot{\rho}_{E\nu} = \left(\frac{1}{3}\nu\frac{\partial \rho_{E\nu}}{\partial \nu} - \rho_{E\nu}\right)\frac{1}{V}\dot{V} \qquad \textbf{(12.40)}$$

for the spectral energy density during an adiabatic change. Since this quantity must be a function of volume and frequency, Equ.(12.40) can be changed to

$$V\frac{\partial \rho_{E\nu}}{\partial V} = \frac{1}{3}\nu\frac{\partial \rho_{E\nu}}{\partial \nu} - \rho_{E\nu} \qquad \textbf{(12.41)}$$

which has the general solution[10]

$$\rho_{E\nu} = \nu^3 f\left(\nu^3 V\right) \qquad \textbf{(12.42)}$$

This result is called *Wien's displacement law*, and holds for every frequency independent of the particular spectral distribution of the radiation. It reduces the complexity of the problem by reducing the spectral densities and intensities to functions of a single argument. (Before, we had to take them as functions of frequency and volume, or as will be shown, of temperature.) The law shows that if we know the distribution for a specific value of the volume, the function *f* may be found which then lets us calculate the spectral energy distribution for any other volume.

If we assume the original spectrum of the radiation in the cavity to be that of blackbody radiation, we can apply the relation between its volume and temperature during adiabatic changes as calculated in Chapter 5 (Section 5.4):

$$T^3 V = constant \tag{12.43}$$

Using this relation, Equ.(12.42) can be transformed into a relation which shows that the spectrum should depend upon the ratio of temperature and frequency:

$$\rho_{E\nu} = \nu^3 f_2\left(\frac{\nu}{T}\right) \tag{12.44}$$

The concrete law found to hold for the spectral distribution of blackbody radiation is indeed of the form suggested by Wien's displacement law; see Equ.(12.50).

12.3.4 Entropy and Temperature of Radiation

Recall what we know about the thermodynamics of blackbody radiation. We can derive the Gibbs fundamental relation for the integral quantities from the results of Section 5.4. The total entropy and energy of radiation inside volume *V* satisfy

$$\dot{S} = \frac{1}{T}\dot{E} + \frac{P}{T}\dot{V} \tag{12.45}$$

According to Equ.(5.76) of Chapter 5, the radiation pressure is one-third the energy density. If we introduce the densities of entropy and of energy, the Gibbs fundamental form becomes

$$\frac{d}{dt}\left(\rho_S V\right) = \frac{1}{T}\frac{d}{dt}\left(\rho_E V\right) + \frac{1}{T}\frac{1}{3}\rho_E \dot{V}$$

Assembling the terms which depend either upon the volume or upon its rate of change, and noting that the latter two quantities are independent, we end up with the following two results:

---

[10] This may be shown by inserting the result back into the differential equation. The two derivatives of the spectral energy density with respect to volume and to frequency are

$$\frac{\partial \rho_{E\nu}}{\partial V} = \nu^3 \frac{\partial f}{\partial\left(\nu^3 V\right)}\frac{\partial\left(\nu^3 V\right)}{\partial V}$$

$$\frac{\partial \rho_{E\nu}}{\partial \nu} = 3\nu^2 f + \nu^3 \frac{\partial f}{\partial\left(\nu^3 V\right)}\frac{\partial\left(\nu^3 V\right)}{\partial \nu}$$

This shows that Equ.(12.41) is satisfied by the solution given in Equ.(12.42).

$$\rho_S = \frac{4}{3}\frac{1}{T}\rho_E \tag{12.46}$$

$$\dot{\rho}_S = \frac{1}{T}\dot{\rho}_E \tag{12.47}$$

The second of these is the Gibbs fundamental relation for the integral radiation densities. Now, while the total entropy density is a function only of the energy density, its spectral counterpart is a function of both spectral energy density and frequency:

$$\rho_{s\nu} = g\left(\rho_{E\nu}, \nu\right)$$

We therefore can write the rate of change of the spectral entropy density in terms of the rates of change of the independent variables:

$$\dot{\rho}_{s\nu} = \frac{\partial \rho_{s\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu} + \frac{\partial \rho_{s\nu}}{\partial \nu}\dot{\nu}$$

Integration over the entire range of frequencies yields

$$\begin{aligned}\dot{\rho}_S &= \int_\nu \left(\frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu} + \frac{\partial \rho_{S\nu}}{\partial \nu}\dot{\nu}\right)d\nu = \int_\nu \frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu}d\nu + \int_\nu \frac{\partial \rho_{S\nu}}{\partial \nu}\dot{\nu}d\nu \\ &= \int_\nu \frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu}d\nu + \dot{\nu}\int_\nu \frac{\partial \rho_{S\nu}}{\partial \nu}d\nu = \int_\nu \frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu}d\nu + \dot{\nu}\int_{\rho_{s\nu}} d\rho_{S\nu} \\ &= \int_\nu \frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu}d\nu + \dot{\nu}\left[\rho_{S\nu}\left(\nu = \infty\right) - \rho_{S\nu}\left(\nu = 0\right)\right] = \int_\nu \frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu}d\nu\end{aligned}$$

Here, we have used the facts that the rate of change of the frequency is independent of the frequency itself, and that the spectral densities of entropy must vanish both for small and for very large frequencies, because otherwise, its integral would not be finite. If we apply the result to steady-state blackbody radiation, we note that the rate of change of the entropy density should be zero. Since this is true for the rate of change of the energy density as well, the relation

$$0 = \int_\nu \frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}}\dot{\rho}_{E\nu}d\nu$$

yields the result that the derivative of the spectral entropy density with respect to the spectral energy density must be a constant. As a consequence of the Gibbs fundamental relation for the densities, Equ.(12.47), this constant must be the inverse of the temperature of the radiation under consideration:

$$\frac{\partial \rho_{S\nu}}{\partial \rho_{E\nu}} = \frac{1}{T} \tag{12.48}$$

This equation states the law of the spectral distribution of blackbody radiation; if we manage to find the entropy of radiation, we will be able to compute the energy distribution. (This is what Planck set out to do.) While this result was derived for blackbody radiation, it must be of more general importance since, as Planck noted:[11]

> *For since $\rho_{S\nu}$ depends only on $\rho_{E\nu}$ and ν, monochromatic radiation, which is uniform in all directions and has a definite energy density $\rho_{E\nu}$, has also a definite temperature given by $\partial\rho_{S\nu}/\partial\rho_{E\nu} = 1/T$, and, among all conceivable distributions of energy, the normal one is characterized by the fact that the radiations of all frequencies have the same temperature.*

Planck therefore extended the notion of radiation temperature to monochromatic radiation. We may think of this as a result of both the existence of a clear relation between energy and entropy for every color of light, and the fact that rays having different frequencies and traveling in different directions in a cavity without absorbing substances do not interact. Therefore, radiation of any spectral distribution will stay undisturbed inside such a cavity. If you start with blackbody radiation of a given temperature, you may change the spectral values of energy and entropy of all frequencies but one by adding or withdrawing some radiation. The spectral entropy and energy densities of the particular frequency being considered will not change, their relation will still be the same, and we should still associate with it the temperature belonging to the original blackbody radiation.

We can now derive Wien's displacement law for the spectral entropy density of radiation. Equ.(12.44) may be inverted to yield

$$\frac{1}{T} = \frac{1}{\nu} f_3\left(\frac{\rho_{E\nu}}{\nu^3}\right)$$

Since the inverse of the radiation temperature is given by Equ.(12.48), we obtain by integration

$$\rho_{s\nu} = \nu^2 f_4\left(\frac{\rho_{E\nu}}{\nu^3}\right) \tag{12.49}$$

This law has a significance for every frequency, i.e., for every ray of a given color and, therefore, for radiation of arbitrary spectral distribution as well.[12]

12.3.5 Planck's Law of the Spectral Distribution of Blackbody Radiation

At the beginning of this century, Planck managed to derive an expression for the spectral intensity of blackbody radiation on the basis of the newly introduced quantum hypothesis. We shall begin by presenting the result for the spectral energy intensity:

$$i_{Evb}(T,\nu) = \frac{2h\nu^3}{c^2}\frac{1}{e^{h\nu/kT} - 1} \tag{12.50}$$

---

[11] M. Planck (1906), paragraph 93.

[12] The general forms of the laws should contain reference to the speed of light which may be different in different media. Since we have assumed c to be the same in all media, its appearance is not required. See Planck (1906), paragraph 94, for the general forms of the laws.

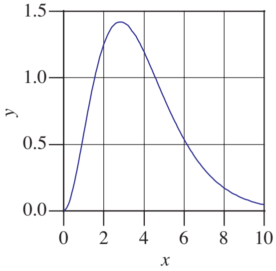


Figure 12.10: The Planck function $x^3/(e^x - 1)$, where $x = h\nu/kT$, is a dimensionless representation of the result shown in Equ.(12.50). The spectral intensity of blackbody radiation as a function of frequency has the same form. Higher temperatures mean higher maxima of the curves and higher values for the frequency of the maxima.

h and k stand for Planck's constant and Boltzmann's constant, respectively. Their numerical values are $h = 6.63 \cdot 10^{-34}$ J · s and $k = 1.38 \cdot 10^{-23}$ J/K. Planck's formula beautifully reflects measurements made of the spectral intensity of blackbody radiation (see Fig. 12.10). The overall intensity of black-body radiation (Equ.(12.6)) may be obtained from Equ.(12.50) by integrating over the entire spectrum. Note that the spectral energy density, which is obtained by virtue of Equ.(12.35), i.e.,

$$\rho_{E\nu b}(T,\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT} - 1} \tag{12.51}$$

has indeed the functional dependence suggested by Wien's displacement law given in Equ.(12.44).

12.3.6 Spectral Entropy Distribution and Temperature of Radiation

The fundamental relationship between the entropy and the energy of radiation which is expressed by Equ.(12.48) lets us calculate the spectral entropy density of radiation as a function of the energy density and of frequency. As you can verify by taking the derivative, $\rho_{S\nu}$ must be given by[13]

$$\rho_{S\nu} = \frac{8\pi k\nu^2}{c^3}\left\{\left(1 + \frac{c^3\rho_{E\nu}}{8\pi h\nu^3}\right)\ln\left(1 + \frac{c^3\rho_{E\nu}}{8\pi h\nu^3}\right) - \frac{c^3\rho_{E\nu}}{8\pi h\nu^3}\ln\frac{c^3\rho_{E\nu}}{8\pi h\nu^3}\right\} \tag{12.52}$$

The index b for blackbody has been removed from the entropy and energy densities. If we assume Equ.(12.51) to hold individually for every frequency, independently of whether the distribution of radiation is that of a black body, then

$$\rho_{E\nu} = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT} - 1} \tag{12.53}$$

also defines a temperature of radiation at frequency ν according to

---

[13] Write Equ.(12.52) in the form

$$\rho_{s\nu} = \frac{1}{b}\frac{k}{h\nu}\left\{\left(1 + b\rho_{E\nu}\right)\ln\left(1 + b\rho_{E\nu}\right) - b\rho_{E\nu}\ln\left(b\rho_{E\nu}\right)\right\} \quad , \quad b = \frac{c^3}{8\pi h\nu^3}$$

The derivative $\partial\rho_{S\nu}/\partial\rho_{E\nu}$ is

$$\frac{\partial\rho_{s\nu}}{\partial\rho_{E\nu}} = \frac{k}{h\nu}\left\{\ln\left(1 + b\rho_{E\nu}\right) - \ln\left(b\rho_{E\nu}\right)\right\} = \frac{k}{h\nu}\ln\left(1 + \frac{1}{b\rho_{E\nu}}\right)$$

which, by Equ.(12.51), is the reciprocal of the absolute temperature of the radiation at frequency ν. If we wish to extend the concept of temperature to monochromatic radiation, as we have implicitly done, we can do so by defining a temperature of light at frequency ν which the ray would have if it were part of an entire blackbody spectrum, i.e., by using Equ.(12.51).

$$T_\nu = \frac{h\nu}{k}\frac{1}{\ln\left(\frac{8\pi h\nu^3}{c^3\rho_{E\nu}}+1\right)} \tag{12.54}$$

We interpret this as the temperature of monochromatic rays. The result will be used in a practical application when we attempt to compute the entropy and the temperature of solar radiation passing through the Earth's atmosphere (Chapter 16).

12.4 POLARIZATION OF RADIATION

Electromagnetic radiation consists of transverse waves. We may construct an image of a wave in which the vector of the electric field vibrates in a definite plane that also contains the direction of propagation of that wave, as in Fig. 12.11. Such a wave is said to be *plane polarized*. A ray of unpolarized light, such as undisturbed blackbody radiation, consists of waves with a random distribution of planes of vibration of the electric field. Viewed head on, completely polarized and unpolarized light would appear as presented at the bottom of Fig. 12.11.

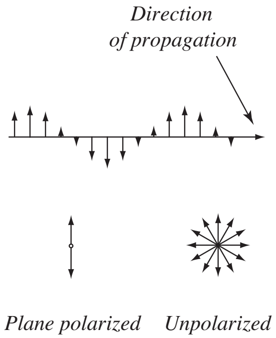


Figure 12.11: Electromagnetic radiation consists of waves with the electric field vibrating in particular planes. Plane polarized light consists of waves which have only a single plane of vibration, while unpolarized radiation consists of waves with randomly oriented planes.

Originally unpolarized radiation may become (partly) polarized as a result of several types of processes. Reflection, double refraction in calcite crystals, passage through polarizing sheets, and scattering are all sources of polarized light. It is found that the intensity of a beam of radiation in any state of polarization can be calculated as the sum of two plane polarized components where the planes must be perpendicular to each other but can otherwise have an arbitrary orientation. If we use the notation i_ν for the intensity of a plane polarized component, we can say that

$$\begin{aligned} i_\nu' &= i_\nu^{max}\cos^2\varphi + i_\nu^{min}\sin^2\varphi \\ i_\nu'' &= i_\nu^{max}\sin^2\varphi + i_\nu^{min}\cos^2\varphi \end{aligned} \tag{12.55}$$

and

$$i_\nu = i_\nu' + i_\nu'' = i_\nu^{max} + i_\nu^{min} \tag{12.56}$$

The intensity of the beam is independent of the orientation φ of the planes of polarization. i^{max} and i^{min}, which are the maximum and minimum values attained by two perpendicular plane-polarized components, are called the principal values of the intensity Their respective planes are called the principal planes of vibration. These relations hold for the energy intensity, and for the entropy intensity for independent (noncoherent)[14] components. For example, the integral intensities of entropy and of energy are calculated in terms of

---

[14] If the light is (partly) coherent, the entropy intensity calculated from arbitrary components is larger than the sum of the entropy intensities associated with the principal planes of polarization. See Planck (1906), p. 100–102.

$$
\begin{aligned}
i_S &= \int_\nu \left(\mathrm{i}_{S\nu}^{max} + \mathrm{i}_{S\nu}^{min} \right) d\nu \\
i_E &= \int_\nu \left(\mathrm{i}_{E\nu}^{max} + \mathrm{i}_{E\nu}^{min} \right) d\nu
\end{aligned}
\qquad \textbf{(12.57)}
$$

Now, the spectral values of the single (principal) components are computed using the following relations:

$$
\mathrm{i}_{E\nu} = \frac{h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1} \qquad \textbf{(12.58)}
$$

$$
\mathrm{i}_{S\nu} = \frac{k\nu^2}{c^2} \left\{ \left(1 + \frac{c^2 \mathrm{i}_{E\nu}}{2h\nu^3} \right) \ln\left(1 + \frac{c^2 \mathrm{i}_{E\nu}}{2h\nu^3} \right) - \frac{c^2 \mathrm{i}_{E\nu}}{2h\nu^3} \ln \frac{c^2 \mathrm{i}_{E\nu}}{2h\nu^3} \right\} \qquad \textbf{(12.59)}
$$

where *i* stands for either of the two principal components. For an arbitrary state of polarization, we introduce the degree of polarization *P* and calculate

$$
\begin{aligned}
\mathrm{i}_{E\nu}^{min} &= i_{E\nu} \frac{1}{2} (1 - P) \\
\mathrm{i}_{E\nu}^{max} &= i_{E\nu} \frac{1}{2} (1 + P)
\end{aligned}
\qquad \textbf{(12.60)}
$$

These values are then inserted in Equ.(12.59), from which we can calculate the entropy and the temperature of polarized radiation.

EXERCISES AND PROBLEMS

1. The intensity of solar radiation. (a) Derive the intensity with respect to energy of solar radiation near the Earth. The energy flux density of the Sun's radiation at the Earth is 1360 W/m^2 (the *solar constant*). The Sun's radius is $7.0 \cdot 10^8$ m, and its distance from the Earth is $1.5 \cdot 10^{11}$ m (one astronomical unit). (b) If you consider this to be the intensity of blackbody radiation, what is its equivalent temperature? Compare the result to the surface temperature of the Sun, which from spectroscopic measurements, is known to be 5780 K. What is the importance of this result? (c) Derive the relation between the intensity with respect to entropy and with respect to energy for blackbody radiation. Compute the entropy flux density of solar radiation at the Earth's distance.
2. Hemispherical flux density of blackbody radiation. (a) Apply the result for the hemispherical flux density of isotropic radiation to blackbody radiation, i.e., derive Equ.(12.9). (b) Compute the numerical values of the hemispherical energy flux density of radiation at the surface of the Sun and inside an oven which is kept at a temperature of 300°C.
3. The radiation shape factor for two disks (Fig. P.3). Compute the radiation shape factor F_{12} for two disks perpendicular to the same center line. Assume the first disk to be very small, having a surface area A_1, while the second disk has radius R. Show that it is equal to

$$
F_{12} = \frac{R^2}{R^2 + d^2}
$$

How large is the shape factor F_{21}?

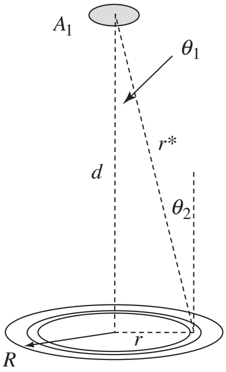


Figure P.3

4. Radiation networks: gray surfaces and shape factors. Assume the disks of Problem 3 to have gray surfaces with absorptivities a_1 and a_2, respectively. Calculate the rate of transfer

of energy between the bodies if their temperatures are T_1 and T_2, respectively. Show that the surface characteristics and the geometrical arrangement may be written in the form of resistances. Their combined influence is represented by the sum of the three resistances. Compute a numerical result for the energy flux for two disks 1.0 m apart, the first with a surface area of 0.50 m^2, the second with an area of 0.010 m^2. Assume their temperatures to be 1000°C and 20°C, respectively. The larger of the surfaces has an absorptivity of 0.95, while that of the smaller one is 0.30.

5. Extinction of a ray of light. (a) Consider a cube of length Δx and surface area A filled with a fluid. A narrow cone of light passes through the surface A. Show that the coefficient of absorption is the fractional change of the intensity of radiation per unit length. (b) The attenuation (extinction) of a ray of light is due to both absorption and scattering. The scattering coefficient β is defined in the same manner as the coefficient of absorption. Derive the differential equation for the intensity of light as a function of position x along the ray. (c) The intensity measured in terms of energy of a ray of light is attenuated to half its value when passing through 20 km of air. Compute the average of the sum of coefficients of absorption and scattering (with respect to energy).

6. Mass absorption coefficient and the diffusion of radiation. The mass absorption coefficient (opacity) κ_ρ of matter is defined as the fraction of radiant energy absorbed divided by the mass density. To be precise, it is defined by the law of absorption:

$$\frac{dj}{dx} = -\kappa_\rho \rho j$$

In other words, the opacity and the mean free path must be related by

$$l_{mean} \sim \left(\kappa_\rho \rho\right)^{-1}$$

The numerical factor in this relation is of the order of unity. Compute a rough value of the mean free path and the opacity of stellar material. Take a star, such as our Sun, with a central temperature of 15 million K, a radius of 700000 km, a mass of $2 \cdot 10^{30}$ kg, and a net energy flux of $4 \cdot 10^{26}$ W. Estimate the quantities for a median point inside the star.

7. The blackbody spectrum in terms of the wavelength. (a) Derive the formula for the spectral energy intensity of blackbody radiation in terms of wavelength and present a nondimensional form of the result, as was done for the frequency distribution in Fig. 12.10. (b) Determine the location of the maximum of the spectral distribution and give the numerical result for the radiation of the Sun if it is interpreted as blackbody radiation at 5780 K. (c) Derive the expression for the spectral entropy intensity with wavelength as the independent variable.

8. Converting monochromatic light to blackbody radiation. Consider sunlight which is passed through a filter that blocks out radiation except for a narrow band of frequencies $\Delta \nu$. The light of the Sun has a temperature T_s = 5800 K. The filtered ray is allowed to pass into a cavity where it is converted to blackbody radiation. (a) Calculate the temperature of the resulting blackbody radiation assuming the frequency interval of the filtered light lies between 490 nm and 500 nm. (b) How much entropy has been produced in the process?

9. Consider the transport of heat with radiation in the interior of a star which we model as being in spherically symmetric hydrostatic equilibrium; changes of volume of the gas are assumed not to disturb this situation. Nuclear reactions release energy, with the source rate given by the specific rate $\sigma_{E,r}$ (i.e., the rate divided by the mass). The luminosity $L(r)$ is the total energy flux penetrating the spherical surface at radius r. (a) Model stellar matter as a simple fluid and show that the rate of change of the specific entropy s (entropy per mass) must be given by

$$T\dot{s} = \sigma_{E,r} - \frac{\partial L}{\partial m}$$

Here, the independent variable has been changed to the mass $m(r)$ inside the sphere of radius r. (b) Show that the gradient of the luminosity $\partial L / \partial m$ is given by

$$\frac{\partial L}{\partial m} = \sigma_{E,r} - \frac{3}{2}\rho^{2/3}\frac{d}{dt}\left(\frac{P}{\rho^{5/3}}\right)$$

for a monatomic ideal gas. (c) Show that the gradient of luminosity inside a star is determined by the source rate due to reactions only if steady-state conditions prevail.

10. The precise definition of the mass absorption coefficient for diffusion of radiation through matter, i.e., the opacity κ_ρ (Problem 6), actually is given by

$$l_{mean} = \frac{4}{3}\frac{1}{\kappa_\rho \rho}$$

where l_{mean} is the mean distance travelled by radiation before being absorbed. Show that the luminosity inside a star where all the energy is transported by radiation is given by

$$L(r) = -\frac{64}{3}\pi\sigma\frac{r^2T^3}{\kappa_\rho \rho}\frac{dT}{dr}$$

PART IV

SPECIAL PROCESSES AND SYSTEMS

CHAPTER 13

CONDUCTION AND COUPLED TRANSPORTS

Conductive phenomena are ubiquitous in nature and in technical and social systems. We have already seen and discussed examples of uniform models of conduction in fluids and electricity (Chapter 1), in mechanics (Chapter 3), heat (Chapter 4), and chemical processes (Chapter 6). Finally, the foundation was laid for the treatment of conduction in continuous models (Chapter 11).

Conductive transports are not only important and interesting for their applications, they also are fundamental for our understanding of energy in models of physical processes. Among the transport processes—conduction, convection, and radiation—only the first relates directly to the notion of power which has been so important in the formulation of the theory of the dynamics of heat: the power of a conductive current of entropy is determined by this current and the temperature difference by which it is effected. Furthermore, conductive transports of different fluidlike quantities such as entropy, charge, and amount of substance, are coupled in important ways leading to phenomena such as themoelectricity and thermodiffusion.

In this chapter, I will develop the theory of the conduction of entropy in a single spatial dimension. This is simpler than the treatment of continuum thermodynamics demonstrated in Chapter 11, which should allow us to formulate some models in detail and actually solve them. Subsequently, a question will be raised which has vexed theories of conduction: in theory, conductive transports are infinitely fast. A simple model of the conduction of entropy will be presented where transport speeds are finite—the model makes use of the idea of inductive processes. Finally, thermoelectricity will be introduced more formally than in Chapter 4. This will serve as an example of how to deal with coupled conductive phenomena.

13.1 THE BALANCE OF ENTROPY IN A SINGLE DIMENSION

Here, the equation of balance of entropy for a single spatial dimension will be developed. Applications to conduction will be discussed in Section 13.2. Basically, the equations have been derived before, first for the phenomena involving a biological species—locust living in a single-dimensional space (Section 11.1)—and then for the transport of entropy under fairly general circumstances (Section 11.4). It makes sense to repeat the derivation for entropy in a single dimension, just to get better acquainted with the formulation of spatially continuous models. This should also prepare us for solving some simple examples by hand.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_14,

13.1.1 Current Density and Flux of Entropy

As before, we take the step from uniform to continuous models by introducing spatially distributed quantities—the densities of entropy currents over a surface and the density of entropy inside a body. Let me begin with currents. In a single dimension, the component of the *entropy current density* vector obviously has a distinct sign depending upon the direction of flow with respect to the choice of positive coordinate (see Fig. 13.1). This sign is independent of the body and the surface through which entropy is flowing.

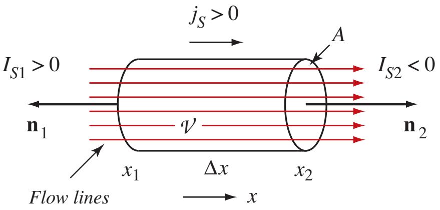


Figure 13.1: A one-dimensional current cuts through a body with plane surfaces perpendicular to the flow of heat. A flux I_S is associated with each surface. Its sign tells us whether the current is flowing into or out of the body.

As you know, we also need a quantity related to flows which allows us to do the accounting for entropy with respect to a chosen body. We have to be able to tell how much entropy is flowing across the entire surface or parts thereof. For this reason, we introduce the *entropy flux* I_S which is a signed scalar quantity defined with respect to a body and (a part of) its surface. In the simple one-dimensional case depicted in Fig. 13.1, the magnitude of the entropy flux must be given by the product of the current density and the surface area. To make the definition precise, we have to introduce the orientation of the surface of a body, using a unit vector **n** perpendicular to the surface at every point and pointing outward, i.e., away from the body under consideration (Fig. 13.1). With this vector, the flux of entropy through either of the two surfaces of the body cut by the current in Fig. 13.1 is given by the scalar product

$$I_S = -A\,\mathbf{j}_S \cdot \mathbf{n} \tag{13.1}$$

In other words, we count the flux as a positive quantity if the current is flowing into the body. The net flux is computed by the sum over discrete parts of the surface:

$$I_{S,net} = -\sum_{i=1}^{N} A_i \mathbf{j}_{Si} \cdot \mathbf{n}_i \tag{13.2}$$

In the case depicted in Fig. 13.1, the net flux is

$$I_{S,net} = -A\Big(j_S(x+\Delta x) - j_S(x)\Big) \tag{13.3}$$

13.1.2 Steady-State Balance of Entropy for a Continuous Body

Let us derive the differential form of the law of balance of entropy in conductive transport. This is necessary since we want to obtain conditions for every point inside a body as befits a theory describing a continuum. We start from the equation of balance of entropy for a *body*. In the steady state, the net current must be equal to the production rate of entropy:

$$0 = I_S + \Pi_S \tag{13.4}$$

This much we can read from the equation of balance of entropy for conduction, as in Equ.(7.1), by setting the rate of change of the entropy content equal to zero. The derivation, which in one dimension is a very simple example of the more general case, proceeds as follows: We express the quantities in Equ.(13.4) in terms of integrals of densities over the body. Let us start with the flux of entropy. It expresses the net rate of flow of entropy across the surface of the body. Above, we introduced the *current density*, which describes the distribution of the current over the boundary. Obviously, we will obtain the net flux if we integrate the current density over the surface of the system:

$$I_S = -\int_{\mathcal{A}} j_S \, dA \tag{13.5}$$

$\mathcal{A}$ is the closed surface of the body. In the one-dimensional case the current density is a function of the position variable x only. Since entropy flows only in the x-direction, the integral over the surface is strongly simplified. There are contributions only from the flow across the faces of the body (Fig. 13.1).

Now we proceed to derive the rate of production of entropy for the entire body in terms of a *production density*. Since the production of entropy takes place inside a body, it is a volumetric process. A density is the proper quantity for expressing such a phenomenon. The production rate for the body is given simply by the integral of the associated density over the volume:

$$\Pi_S = \int_{\mathcal{V}} \pi_S \, dV \tag{13.6}$$

Here, π_S is the *density of the rate of generation of entropy* in the body, and $\mathcal{V}$ is the volume. Next, we change the variable of integration to the volume in Fig. 13.5. This is achieved by replacing the current density by its derivative with respect to x, and integrating over x as well. Because of the balance of entropy we set the result equal to the expression in Equ.(13.6):

$$\int_{\mathcal{V}} \frac{dj_S}{dx} dx \, dA = \int_{\mathcal{V}} \pi_S \, dV \tag{13.7}$$

or

$$\int_{\mathcal{V}} \left[\frac{dj_S}{dx} - \pi_S \right] dV = 0 \tag{13.8}$$

Note that the expression $dx\,dA$ is equal to dV. This equation lets us draw an important conclusion: The integral can be equal to zero under all circumstances only if the integrand is identical to zero. This means that

$$\frac{dj_S}{dx} = \pi_S \tag{13.9}$$

which is *the differential form of the equation of balance of entropy in the steady state* for one-dimensional flow. It holds at every point of the body, and not just as an overall expression for the entire body. It expresses a simple idea, namely, that the spatial rate of change of a current of a nonconserved quantity depends upon the rate at which this quantity is produced at every point. Obviously then, the spatial rate of change of a conserved quantity in one-dimensional flow should be zero.

13.1.3 Balance of Entropy for Conduction and Supply

In Section 7.4.2, we first came across the mode of transfer in which entropy appears inside bodies without flowing over system boundaries via currents, and without being created in the system. This is the case in radiative transfer, which we have modeled using sources (or sinks) of entropy inside a body.

Another important class of sources of entropy are chemical and nuclear reactions. Normal fires, and the fires inside stars which are driven by nuclear reactions, create vast amounts of entropy. If we do not count the entropy and energy they release to be part of the system under consideration, entropy and energy are effectively added from outside. Looked at this way, entropy is not created in the system, which means that there must be source rates, rather than production rates of entropy which account for these processes.

In this section we will discuss the role of source terms in the equation of balance of entropy. At the same time, we will ask about the role of energy in the processes just listed. The description will be limited to one-dimensional steady state cases. We will assume entropy to appear or disappear at every point of a body, while it is transported through the body by conduction.

Entropy supply. We have already seen instances of how the increase of entropy inside a system without transport across surfaces is described mathematically. One way of adding entropy is by production. Irreversibility appears in the equation of balance of entropy by way of the production rate, as seen in Equations (7.1) or (7.2). The particular case associated with the conduction of heat is described by a production rate per volume π_S, which will be derived in Equ.(13.24). The second possibility, i.e., sources and sinks of entropy, is modeled in an analogous manner. This is evident in the case of radiation, where a source rate was first introduced in Equ.(7.5).

Mathematically, there is no difference between production and source terms in the equation of balance of entropy. Physically, this means that either type of process leads to the appearance (or possibly the disappearance) of entropy in a way which cannot be described by currents across surfaces, but must be modeled as sources or sinks.

Balance of entropy. For a formal derivation of the laws governing conduction with supply, we can start with the equation of balance, which holds for the entire body under steady-state conditions:

$$0 = I_S + \Pi_S + \Sigma_S \tag{13.10}$$

The term Σ_S describes all effects of the supply of entropy. Proceeding as we did in Section 13.1.2, this becomes

$$\int_{\mathcal{A}} j_S \, dA = \int_{\mathcal{V}} \pi_S \, dV + \int_{\mathcal{V}} \sigma_S \, dV \tag{13.11}$$

Transformation of the integrals leads to

$$\frac{dj_S}{dx} = \pi_S + \sigma_S \tag{13.12}$$

13.1.4 Balance of Entropy in Time-Dependent Conduction

The interaction of storage and flow of entropy is the most general problem we are confronted with in thermodynamics. In steady-state transport processes, bodies lose as much entropy by outflow as they gain by production and inflow. If the transport processes are to change in time, it must be due to the change of the amounts of entropy and energy which are stored in systems. In other words, the properties of bodies (which might be described by the entropy capacitance and the latent entropy) are responsible for the existence of dynamical processes.

Consider bodies that conduct heat. If the amount of stored entropy is allowed to change, we are dealing with time-dependent conduction. The proper equation of balance of entropy for an extended body conducting heat is

$$\dot{S} = I_S + \Pi_S \tag{13.13}$$

The difference between this and Equ.(13.4) is the appearance of the time rate of change of the entropy of the body.

Now we will derive the differential form of the equation of balance. (Recall the procedure of Section 13.1.2.) All three quantities appearing in Equ.(13.13) are integrals of associated quantities which vary from point to point in a body. Remember that a surface density is associated with the flux of entropy I_S. This surface density is the flux density. If this quantity is integrated over the surface, the flux is recovered. We obtain the rate of production of entropy, on the other hand, if we integrate the density of the rate of production over the volume of the body. (See Equ.(13.6).)

In the same manner, a *density of entropy* ρ_S is associated with the entropy of a body. Just as the mass of a body is obtained by integrating the mass density over the volume, we recover the entropy of the body by evaluating the integral of the density of entropy over the volume:

$$S = \int_{\mathcal{V}} \rho_S \, dV \tag{13.14}$$

If we insert the integral expressions listed above into the law of balance of entropy in Equ.(13.13), we arrive at

$$\frac{d}{dt}\int_{\mathcal{V}} \rho_S \, dV = -\int_{\mathcal{A}} j_S \, dA + \int_{\mathcal{V}} \pi_S \, dV \tag{13.15}$$

This equation must be transformed somewhat to yield the final differential form we are looking for. Since we are treating conduction through stationary bodies, the volume under consideration does not change with time. Therefore, we may place the time derivative in the left-hand side under the integral. The first term on the right is transformed as in Equ.(13.7). All of these changes lead to

$$\int_{\mathcal{V}} \frac{\partial \rho_S}{\partial t} dV = -\int_{\mathcal{V}} \frac{\partial j_S}{\partial x} dx \, dA + \int_{\mathcal{V}} \pi_S \, dV$$

Now all three terms may be combined:

$$\int_{\mathcal{V}}\left[\frac{\partial \rho_S}{\partial t}+\frac{\partial j_S}{\partial x}-\pi_S\right]dV=0 \tag{13.16}$$

For the same reason given after Equ.(13.8), the expression in the integral must be zero for all values of the independent variables. The resulting equation is the differential form of the equation of balance of entropy for time-dependent, one-dimensional conduction:

$$\frac{\partial \rho_S}{\partial t}+\frac{\partial j_S}{\partial x}=\pi_S \tag{13.17}$$

Since we have two independent variables, namely time and position in the x-direction, the equation is a partial differential equation. The first term is due to the storage of entropy, and the second one describes conduction, while the third (on the right-hand side) is responsible for the production of entropy.

QUESTIONS

1. What quantities are introduced to describe (a) the distribution of entropy in a body, (b) the distribution of a current of entropy over a surface, (c) the distribution of an entropy production rate inside a body?
2. The orientation of the surface of a body is assumed to be positive for the outward direction. How do you ensure that the flux of entropy is counted as a positive quantity for a current flowing *into* the body?
3. Consider single-dimensional steady-state conduction of entropy. Why is the divergence of the entropy current density not equal to zero?
4. How would you distinguish between entropy source rates and entropy production rates?

EXAMPLE 13.1. Dynamical law of balance of entropy for conduction and supply.

What is the dynamical form of the law of balance of entropy (in a single spatial dimension) if the supply of entropy (such as in radiation) is included?

SOLUTION: The derivation of this form of the equation of balance is a simple extension of what was derived in Section 13.1.3 and Section 13.1.4. The balance of entropy for an entire body is

$$\dot{S}=I_S+\Pi_S+\Sigma_S$$

If densities are introduced, we obtain

$$\int_{\mathcal{V}}\frac{\partial \rho_S}{\partial t}dV=-\int_{\mathcal{A}} j_S\,dA+\int_{\mathcal{V}}\left(\pi_S+\sigma_S\right)dV$$

which the leads to

$$\frac{\partial \rho_S}{\partial t}+\frac{\partial j_S}{\partial x}=\pi_S+\sigma_S$$

This demonstrates that—purely on the basis of the law of balance—we cannot distinguish between sources and production of entropy.

13.2 CONSTITUTIVE THEORY OF CONDUCTION IN A SINGLE DIMENSION

In this section we shall turn to the discussion of the constitutive theory of conduction. Entropy flows from warmer to cooler places. It is therefore impossible for bodies which conduct heat to be homogeneous as far as temperature is concerned. We have to give every point of a body its own temperature which may differ from temperatures at arbitrarily close neighboring points. Such an approach is called a *field description* of the phenomenon.

A body that conducts entropy undergoes changes of shape and volume, and parts of it may flow relative to other parts. The description of these processes is rather complex. Therefore, at this point, we will treat only the simplest possible case of conductive transport—the flow of entropy through an otherwise unchanging body. We will call this situation *pure conduction* of heat. Thus, the only independent variable of our theory, apart from time, will be the temperature which is now a function of time and position.

It turns out that we need three additional pieces of information to complete the standard model of thermal conduction: an expression for the flow of entropy in terms of spatial changes of temperature,[1] another expression for the relationship between temperature and entropy density, and the energy principle relating to thermal processes.

13.2.1 Fourier's Law of Conduction of Entropy

We have seen twice before (in Chapters 7 and 11) that a simple assumption as to how a conductive current of entropy depends upon circumstances leads to good models of the transport of entropy in conduction. In Equ.(7.14), we already derived the form of this assumption, which is called Fourier's law, for the spatially continuous case:

$$j_S = -k_S \frac{dT}{dx} \tag{13.18}$$

If you imagine the spatially varying temperature in a body to create something like a thermal landscape, Fourier's law expresses the idea that the flow of entropy at a given point depends upon how steep the slope of this field is, i.e., the *temperature gradient* *dT/dx*, and upon local properties, i.e. the *entropy conductivity* *k_S*.

In Chapter 11 (Equ.(11.90) in Section 11.8.6) we were able to derive the relation between the current densities of entropy and energy in conduction:

$$j_E = T j_S \tag{13.19}$$

T is the local temperature. This means that the thermal conductivity with respect to energy, k_E, is given by the product of the temperature of a material and its entropy conductivity. Note that Equ.(13.19) is the local equivalent of what we have taken for granted in our description of uniform dynamical systems in Part II of the book.

---

[1] It turns out that the simplest model of a current of entropy—Fourier's law—predicts infinite speeds of propagation of conductive disturbances. Later in this chapter, we will see what it takes to get a result that is more physically appealing.

13.2.2 The Balance of Energy in Conduction of Entropy

We still need the law of balance of energy for a body undergoing conduction. If we neglect all other processes except the conductive flow of entropy, there is only one energy flow term in the law of balance:

$$\dot{E} = I_{E,th} \tag{13.20}$$

Just as for entropy, this equation can be transformed so that it applies to the spatially continuous case. Terms for the energy density, ρ_E, and the (conductive thermal) energy current density, j_E, are introduced and related to the overall quantities. Transforming Equ.(13.20) leads to:

$$\frac{\partial \rho_E}{\partial t} + \frac{\partial j_E}{\partial x} = 0 \tag{13.21}$$

Equ.(13.17) shows that we arrive at this result for a quantity that does not admit production. This is the differential form of the law of balance of energy, which now replaces the overall balance in Equ.(13.20). We will see how this law, together with the relationship between fluxes of entropy and energy (Equ.(13.19)), leads to a determination of the density of the production of entropy in Equ.(13.9).

13.2.3 The Generation of Entropy in Conduction

With Fourier's law, we have solved only one part of the problem of the balance of entropy. Since entropy is produced in conductive transport, we still need an expression for the production term in the equation of balance. The problem will be solved for steady-state processes. Actually, as we have seen in Chapter 11, the result holds for general processes as well.

The result is a consequence of the combination of the laws of balance of entropy and energy. As before, we will consider purely one-dimensional flow of heat (Fig. 13.1). The relationship between the fluxes of entropy and energy (Equ.(13.19)) leads to

$$\frac{d}{dx}\left(T\, j_S\right) = T\,\frac{dj_S}{dx} + j_S\,\frac{dT}{dx} \tag{13.22}$$

According to the steady-state balance of energy, this expression is equal to zero. As a consequence we have

$$\frac{dj_S}{dx} = -\frac{1}{T}\, j_S\,\frac{dT}{dx} \tag{13.23}$$

Comparison to Equ.(13.9) demonstrates that the density of production of entropy in conduction takes the form:

$$\pi_S = -\frac{1}{T}\, j_S\,\frac{dT}{dx} \tag{13.24}$$

Let us develop a graphical interpretation of this result. Where does the energy come from for the production of entropy in the case of conduction? We can use the image of entropy flowing from a higher level to a lower one just as we did in the case of operating a heat engine. The waterfall picture used for heat engines also applies to our current case: entropy falling from a higher to a lower temperature releases energy for a follow-up process. Something, however, must be vitally different in the cases of conduction of heat and the operation of a heat engine. No directly visible process is driven by the energy released in the fall of entropy if heat is transported conductively. There are no mechanical, electrical, or other phenomena occurring. So what is happening to the energy released when entropy flows from points of higher to points of lower thermal potential? The energy must be used for something, even if we cannot see it right away.

We know the answer to this question. In the conduction of heat, the energy is used to produce entropy; i.e., the energy drives a thermal process, not a mechanical or an electrical one. You might say that the energy flowing through a body has been "enriched" with more entropy; that is all. This is not as unusual as might appear at first. We can compare the conduction of heat to a number of different processes sharing the same fundamental property. The flow of electrical charge through a resistor, the flow of gas (as in the free expansion of air), or the flow of momentum between two bodies rubbing against each other, are all examples of the class of processes in which the energy released drives entropy production. Since we often say that heat is produced by friction, we can interpret the conduction of heat as a case of "thermal friction." Just as in the other cases, the rate of entropy production is given by the ratio of the rate at which energy is dissipated, and the temperature at which the process is taking place (the term $j_S\, dT/dx$ in Equ.(13.24) is the density of the dissipation rate of energy).

13.2.4 The Field Equation for Temperature

The conduction of heat has forced us to change the description of thermal processes from single values of temperature to fields of temperature. In a body which transports heat conductively, the temperature changes from point to point. (If we do not consider steady-state conditions, it also changes in time.) Here, we will derive an equation governing the field of temperature in steady-state conduction. Such an equation is a *field equation*, which as we shall see, follows from the fundamental law of balance of entropy combined with the particular constitutive law describing conduction (i.e., Fourier's law).

Fourier's law for the current density of entropy will be cast in a form using the conductivity with respect to energy:

$$j_S = -\frac{k_E}{T}\frac{dT}{dx} \tag{13.25}$$

First, we need the spatial derivative of this expression:

$$\begin{aligned}\frac{dj_S}{dx} &= -\frac{d}{dx}\left(\frac{k_E}{T}\frac{dT}{dx}\right)\\ &= -\frac{k_E}{T}\frac{d^2T}{dx^2} - \frac{1}{T}\frac{dT}{dx}\frac{dk_E}{dx} + \frac{k_E}{T^2}\left(\frac{dT}{dx}\right)^2\end{aligned}$$

which according to the equation of balance of entropy, Equ.(13.9), must be the production density of entropy which, in turn, is given by Equ.(13.24). With the current density replaced by Fourier's law, the latter quantity becomes

$$
\begin{aligned}
-\frac{1}{T} j_S \frac{dT}{dx} &= \frac{1}{T}\left(\frac{k_E}{T}\frac{dT}{dx}\right)\frac{dT}{dx} \\
&= k_E \frac{1}{T^2}\left(\frac{dT}{dx}\right)^2
\end{aligned}
$$

According to the equation of balance of entropy we get the following result:

$$
\frac{k_E}{T}\frac{d^2T}{dx^2} + \frac{1}{T}\frac{dT}{dx}\frac{dk_E}{dx} = 0
$$

which is equivalent to

$$
\frac{d}{dx}\left(k_E \frac{dT}{dx}\right) = 0 \tag{13.26}
$$

This equation is the one-dimensional field equation for temperature in steady-state heat conduction.

13.2.5 Supply of Energy and Entropy

In steady-state, and if supply is included, the balance of energy takes a rather simple form. In the absence of energy sources, the spatial rate of change of the energy current density is zero since energy is not generated. Now, however, we have sources which lead to the following *equation of balance of energy* in the steady state:

$$
\frac{dj_E}{dx} = \sigma_E \tag{13.27}
$$

A key point in thermodynamics concerns the relationship between sources of entropy and of energy. When entropy is supplied to a body which has a particular temperature, a definite amount of energy must be supplied as well. Our discussion so far suggests that the constitutive relation between currents of entropy and of energy, and between dissipation rate and production rate should carry over to the supply of entropy and energy as well:

$$
\sigma_E = T\sigma_S \tag{13.28}
$$

σ_E is the density of the rate at which energy is supplied to the body from some other system. We can motivate this relation on the basis of the constitutive theory of simple fluids provided in Chapter 5. In a homogeneous body, the Gibbs fundamental relation tells us that the energy increases at T times the rate of increase of entropy. If there are only sources of entropy, then Equ.(13.28) directly follows for such fluids.

13.2.6 The Field Equation for Temperature in Conduction with Supply

We can prove Equ.(13.28) to be correct by deriving the field equation for temperature from the equation of balance of entropy. The balance of entropy with supply (see Equ.(13.12)), Fourier's law, and Equ.(13.24) yield

$$\frac{d}{dx}\left(-\frac{k_E}{T}\frac{dT}{dx}\right)=\frac{1}{T^2}k_E\left(\frac{dT}{dx}\right)^2+\sigma_S \tag{13.29}$$

This becomes the *field equation for temperature* in the presence of entropy sources:

$$\frac{d}{dx}\left(k_E\frac{dT}{dx}\right)=-T\sigma_S \tag{13.30}$$

The same field equation derived from the balance of energy yields

$$\frac{d}{dx}\left(k_E\frac{dT}{dx}\right)=-\sigma_E \tag{13.31}$$

which is equivalent to Equ.(13.30) if and only if the relationship between sources of entropy and energy is given by Equ.(13.28).

QUESTIONS

5. Consider the law of balance of entropy in Equ.(13.17). Which constitutive laws, and how many of them, are required to complete a model of time dependent conduction?
6. Why is there a negative sign in Fourier's law of conduction? Can one compare this expression to Ohm's law for the conduction of charge? What is the multidimensional form of Fourier's law?
7. Is the entropy production rate in Equ.(13.24) always non-negative?
8. What condition does k_E have to satisfy for the temperature gradient in one-dimensional conduction (steady-state, no supply) to be constant?

EXAMPLE 13.2. The temperature gradient in a bar.

(a) Assume the thermal conductivity with respect to energy, i.e., the factor k_E, to be independent of temperature. Determine the temperature in a long bar as a function of the position in the bar. The values of the temperature are T_u and T_l at the upper and the lower faces of the bar, respectively. (b) What is the solution if the conductivity k_S is constant?

SOLUTION: (a) If the conductivity with respect to energy is constant, the field equation for temperature, Equ.(13.26), becomes

$$k_E\frac{d^2T}{dx^2}=0$$

for constant k_E. This demonstrates that the temperature must be a linear function of the position in the bar, which leads to

$$T(x)=T_u+(T_l-T_u)\frac{x}{L}$$

where L is the length of the bar, and x is measured from the hotter end. Note that the temperature decreases linearly along the bar, a result which was derived before.

(b) If the conductivity k_S is independent of temperature, the conductivity with respect to energy must be a linear function of temperature, namely

$$k_E = T\,k_S$$

The field equation for temperature tells us that, in this case, the product of the temperature gradient and the temperature must be a constant:

$$T\,k_S\frac{dT}{dx} = constant$$

Integration of this differential equation yields the following result:

$$T^2(x) = T_u^{\,2} + \left(T_l^{\,2} - T_u^{\,2}\right)\frac{x}{L}$$

The boundary conditions are the same as in the first case.

EXAMPLE 13.3. The field equation in spherical symmetry.

Derive the field equation for temperature in steady-state conduction for spherically symmetric heat flow. Determine the temperature as a function of radius in a spherical shell for constant thermal conductivity with respect to energy (k_E).

SOLUTION: As in the previous example, we use the balance of energy. For steady-state conditions, the equation of balance for a spherically symmetric shell reads

$$A(r+\Delta r)\,j_E(r+\Delta r) - A(r)\,j_E(r) = 0$$

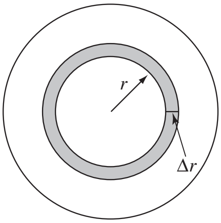


Figure Ex.3

If we insert the expression for the surface area of a sphere, and divide the resulting equation by the volume of the shell, which is equal to

$$V = 4\pi r^2\Delta r$$

we get the following difference equation:

$$\frac{1}{4\pi r^2\Delta r}\left[-4\pi r^2 j_E(r) + 4\pi\left(r^2 + 2r\Delta r + (\Delta r)^2\right)\left(j_E(r) + \Delta j_E\right)\right] = 0$$

If we neglect all higher order terms in Δr and Δj, and after taking the limit for $\Delta r \to 0$, the differential equation of balance for energy in spherical coordinates becomes:

$$\frac{dj_E}{dr} + \frac{2}{r}j_E = 0$$

or

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 j_E\right) = 0$$

To obtain the field equation for temperature, we simply introduce Fourier's Law for the energy current into the equation of balance, which leads to

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 k_E\frac{dT}{dr}\right) = 0$$

If k_E is independent of the temperature, this differential equation yields the following result. The first integration tells us that the product of the radial variable squared and the temperature gradient must be a constant, which will be called – B. Therefore, the temperature is inversely proportional to the radial variable r. The second integration delivers another constant A, and the final result turns out to be

$$T(r) = A + \frac{B}{r}$$

in the shell. The constants A and B are determined by the appropriate boundary conditions.

EXAMPLE 13.4. The temperature in a bar which is heated internally.

Consider a bar of length L and constant conductivity with respect to energy which can conduct heat only in the direction of its axis. It is attached to entropy reservoirs at constant temperatures T_0 and T_L at $x = 0$ and $x = L$, respectively. Let us take $T_0 \geq T_L$. It is heated internally with a constant energy source rate. (This might be due to radioactive heating, as in the previous example.) (a) Determine the steady-state temperature of the bar as a function of position. (b) Would it be possible for the temperature to have a minimum in $0 \leq x \leq L$? (c) Determine the condition for the temperature to decrease monotonically from T_0 to T_L. (d) What is the alternative?

SOLUTION: (a) Under the given conditions the differential equation for the temperature is

$$\frac{d^2T}{dx^2} = -\frac{\sigma_E}{k_E} \quad , \quad \frac{\sigma_E}{k_E} = constant \tag{E1}$$

with boundary conditions

$$T(x = 0) = T_0$$
$$T(x = L) = T_L$$

The solution of Equ.(E1) is a quadratic function which turns out to be

$$T(x) = -\frac{1}{2}\frac{\sigma_E}{k_E}x^2 + \left(\frac{1}{2}\frac{\sigma_E}{k_E}L - \frac{T_0 - T_L}{L}\right)x + T_0 \tag{E2}$$

It is easy to see that for a vanishing source rate the solution turns out to be identical to the one given in Example 13.2, in which case the temperature is a linear function of position.

(b) A quadratic function has an extremum. Here, the second derivative of the temperature with respect to position, i.e., the value of $-\sigma_E/k_E$ is negative, which tells us that the extremum is a maximum, not a minimum. A minimum would be possible only if there were an energy sink instead of a source in the bar.

(c) For the temperature to decrease monotonically from its value at the hotter end, the maximum of the quadratic function obviously must lie outside the range of the bar, i.e., outside $0 \leq x \leq L$. We find the position of the maximum by setting the first derivative of Equ.(E2) equal to zero, which yields

$$-\frac{\sigma_E}{k_E}x_{max} + \frac{1}{2}\frac{\sigma_E}{k_E}L - \frac{T_0 - T_L}{L} = 0$$

Since $T_0 - T_L$ is positive, the position of the maximum may not be larger than $x = L/2$. For this maximum to lie outside the bar it must therefore be negative. This is the case if

$$\frac{\sigma_E}{k_E} < 2\frac{T_0 - T_L}{L^2}$$

We can understand intuitively that the source rate may not be too large for entropy still to be transported from the hotter to the cooler reservoir.

(d) The alternative to the situation just described is the following. The maximum of temperature lies in the range $0 \le x \le L/2$. In this case the temperature gradient is zero or *positive* at the end of the bar which is in contact with the hotter entropy reservoir. Entropy will not flow from the reservoir into the bar; rather, it will flow from the point of maximum temperature inside the bar towards both ends! This happens if

$$\frac{\sigma_E}{k_E} \ge 2\frac{T_0 - T_L}{L^2}$$

i.e., if the source rate of energy becomes large. For increasing values of the source rate, the point of maximum temperature moves towards the middle of the bar. Remember that these considerations hold only for steady state conditions.

EXAMPLE 13.5. The flow of heat through the Earth's mantle, with sources of entropy.

Assume that just about all the entropy which flows out of the surface of the Earth is produced by radioactive decay in the mantle. Calculate the temperature at the base of the mantle if all the entropy is transported conductively. The mantle–core boundary is at a depth of 3400 km. The Earth's radius is 6400 km. Take the conductivity with respect to energy to be constant and equal to 1 W/K · m. The temperature gradient at the surface is 0.06 K/m. Take the surface temperature to be 0°C.

SOLUTION: We can derive the differential equation for temperature in spherical symmetry by going through the same development as in Example 13.3. If we allow for sources, the equation of balance of energy turns out to be

$$\frac{dj_E}{dr} + \frac{2}{r} j_E = \sigma_E$$

If we use Fourier's law we obtain the field equation:

$$k_E\left(\frac{d^2T}{dr^2} + \frac{2}{r}\frac{dT}{dr}\right) = -\sigma_E$$

if the conductivity with respect to energy is constant. This equation can be changed into a simpler one using the following transformation of variables:

$$u = T\,r$$

We obtain

$$\frac{d^2u}{dr^2} = -\frac{\sigma_E}{k_E} r$$

The particular solution of this equation is proportional to the third power of the radius, while the solution of the homogeneous equation is a linear function. Taken together, the solution of this equation is given by

$$u(r) = A\,r^3 + B\,r + C$$

Together with the boundary conditions

$$T(R) = 0$$

$$R\left.\frac{dT}{dr}\right|_R = D$$

we arrive at the following result for the temperature as a function of radius:

$$T(R) = -\frac{1}{6}\frac{\sigma_E}{k_E}r^2 + D + \frac{1}{2}\frac{\sigma_E}{k_E}R^2 - \left(\frac{1}{3}\frac{\sigma_E}{k_E}R^3 + Dr\right)\frac{1}{r}$$

We now need a value for the density of production of energy due to radioactive decay. This rate must be the flux of energy through the surface of the Earth, which can be calculated from the temperature gradient and the conductivity. If we divide this quantity by the volume of the crust we obtain

$$\sigma_E = \frac{4\pi R^2 k_E \left|dT/dr\right|_R}{\frac{4}{3}\pi\left(R^3 - R_{core}^3\right)} = 3.14\cdot 10^{-8}\,\frac{\mathrm{W}}{\mathrm{m}^3}$$

Now the numerical values in the temperature function look like

$$T(R) = -5.2\cdot 10^{-9}r^2 + 2.6\cdot 10^5 - \frac{2.8\cdot 10^{11}}{r}$$

If we insert the value for the radius of the core–mantle boundary, we obtain a temperature of 120,000 K. Even though it is smaller than what we got in Example 7.5, this value is still much too high for the mantle to remain solid. We have made some strongly simplifying assumptions regarding the conductivity and the distribution of the entropy sources. Still it seems rather improbable that entropy can be transported through the mantle of the Earth by conduction alone. In fact, there must be a mechanism much more efficient than conduction, namely, convection.

13.3 TIME DEPENDENT CONDUCTION

The law of balance of entropy for time dependent conduction was already derived in Equ.(13.17) for the case of no supply. Naturally, constitutive relations are needed if we attempt to solve this equation. Here, we must obtain three relations, namely for the density, the flux density, and the density of the production rate of entropy. The last two are known from the previous development of steady state processes. Fourier's law, Equ.(13.18), determines the flux density while the rate of production of entropy is given by Equ.(13.24). So, now we still need to develop the expression for the relation between entropy and temperature for the spatially continuous case.

13.3.1 Capacitive Relation

The form of the constitutive relation for storage of entropy is new. For our present purpose, consider a rigid conductor. Entropy storage is expressed using the entropy capacitance *K* of the rigid body (Equ.(4.39)). We simply have to transform the original definition of the entropy capacitance. For a uniform body, we may do this as follows:

$$V\dot{\rho}_S = V\frac{K}{V}\dot{T} \tag{13.32}$$

The entropy capacitance divided by the volume of the body is the product of the entropy capacitance per mass and the mass density. Therefore, we have

$$\dot{\rho}_S = \rho\kappa\dot{T} \tag{13.33}$$

Here, κ is the specific entropy capacitance of the conductor, and ρ is its density. In general, they are dependent upon the conditions at a particular location.

13.3.2 The Field Equation for Temperature

If this determination is inserted together with Equ.(13.18) and Equ.(13.24) into the equation of balance of entropy, Equ.(13.17), we obtain, after some algebra, the *field equation for temperature* for time-dependent conduction:

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_E \frac{\partial T}{\partial x} \right) \tag{13.34}$$

Instead of the quantities referring to entropy, the temperature coefficient of energy and the conductivity with respect to energy have been introduced.

The result is a partial differential equation for temperature as a function of time and position. Its solution may be very difficult or even impossible to obtain in analytical form. Most often, in practical cases, numerical methods are used to compute a solution. Naturally, the solution is subject to proper initial and boundary conditions. Theories of analytical and numerical solutions of equations such as Equ.(13.34) are beyond the scope of this book. The derivations performed in this section are important simply as examples of how we can deal with the equation of balance of entropy and constitutive relations in somewhat more complicated situations.

EXAMPLE 13.6. Penetration of heat into the upper layers of soil.

What is the effect of periodic changes of temperature at the surfaces of the Earth? How far below the surface can one still notice daily or yearly changes having amplitudes of 7.5 K and 15 K, respectively?

SOLUTION: We need a simplified model of the penetration of heat into the upper layers of the ground. Assume the soil to have a constant temperature (in space and in time) in the absence of the changes at the surface. Model the ground as a body with a plane surface extending infinitely into the vertical direction downward (Fig. Ex.6.1). The material is assumed to have constant properties. These assumptions reduce the problem to one of purely one-dimensional conductive heat transfer, which can be described using Equ.(13.34):

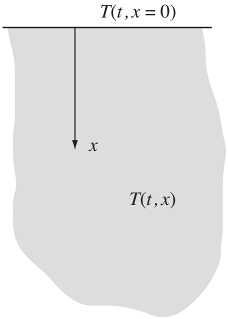


Figure Ex.6.1

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_E \frac{\partial T}{\partial x} \right) \quad \Rightarrow \quad \frac{\partial T}{\partial t} = \frac{k_E}{\rho c} \frac{\partial^2 T}{\partial x^2}$$

The second form holds for constant conductivity. The factor multiplying the spatial derivative of the temperature is called the *thermal diffusivity* α. The field equation for temperature can therefore be written as follows:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

with

$$\alpha = \frac{k_E}{\rho c}$$

The boundary condition at the surface takes the form

$$T(t,0) = T_0 \cos(\omega t)$$

This partial differential equation can be solved as follows. Assume the solution to be separable, which means that we can write

$$T(t,x) = f(t)g(x)$$

Now the differential equation becomes

$$\frac{1}{f(t)}\frac{\partial f(t)}{\partial t} = \frac{\alpha}{g(x)}\frac{\partial^2 g(x)}{\partial x^2}$$

Since we have functions of only one variable on the left and functions of the other on the right, this equation can be satisfied only if each side is a constant *K*, which means that

$$\frac{\partial f(t)}{\partial t} = K f(t)$$
$$\frac{\partial^2 g(x)}{\partial x^2} = \frac{K}{\alpha} g(x)$$

These are ordinary differential equations with simple solutions:

$$f(t) = a \exp(K t)$$
$$g(x) = b \exp\left(\sqrt{\frac{K}{\alpha}} x\right)$$

In summary, the solution of the partial differential equation can be written

$$T(t,x) = T_0 \exp\left(K t + \sqrt{\frac{K}{\alpha}} x\right)$$

The boundary condition at the surface tells us that

$$T_o \exp(K t) = T_o \cos(\omega t)$$

Now, it makes sense to change to the complex domain. Both the real part and the imaginary part of a complex function are solutions of the differential equation. Instead of $K = \omega$, we write $K = i\omega$, which leads to

$$T(t,x) = \mathrm{Re}\left[T_0 \exp\left(i\omega t \pm \sqrt{\frac{i\omega}{\alpha}} x\right)\right]$$

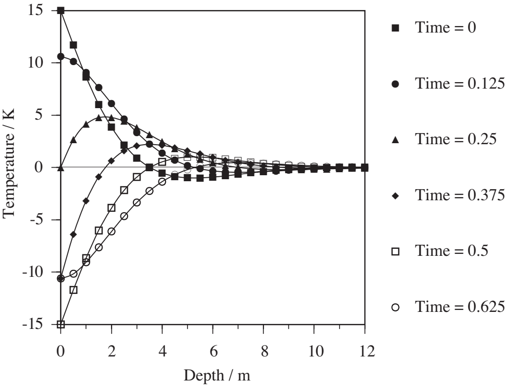
for the real part. This can be transformed into

$$T(t,x) = T_0 \exp\left(-\sqrt{\frac{\omega}{2\alpha}} x\right) \cos\left(\omega t - \sqrt{\frac{\omega}{2\alpha}} x\right)$$

The minus sign must be chosen, since otherwise the temperature would increase with increasing depth.

The graph in Fig. Ex.6.2. shows the solution for a periodic change of temperature at the surface with a period of one year and an amplitude of 15°C. The curves are for different times, where the time is given as a fraction of a year. The thermal diffusivity of the soil was taken to be $5.0 \cdot 10^{-7}$ m^2/s. It is seen that the disturbance decreases to a few degrees some 5 m into the ground. A daily disturbance is felt only to a depth which is about 20 times smaller than for the yearly temperature fluctuation.

Figure Ex.6.2



A periodic climate change with a period of 1 million years, on the other hand, would be felt to a depth of several thousand meters (the curves are similar if the depth variable is scaled as the square root of the period of variation).

13.4 TRANSPORT OF ELECTRICITY

Electricity—electrical charge—can be transported in various ways, such as by ohmic diffusion or by convection. Here, diffusion will be described briefly to prepare the section on thermoelectricity (Section 13.6). Diffusion of charge in ohmic materials can be treated analogously to diffusion of entropy. Moreover, if we add inductive effects, wavelike transports can be discussed which brings up an interesting question when we compare the flow of entropy to that of charge (Section 13.5).

13.4.1 The Law of Balance of Electric Charge

Charge is a scalar fluidlike quantity just like entropy. Indeed, in a couple of respects, its behavior is simpler than that of entropy. Charge cannot be produced or destroyed, and there are no sources of charge due to radiative transports. For these reasons, the law of balance of charge for a body is

$$\dot{Q} = I_{Q,cond,net} \tag{13.35}$$

if we neglect convective flows. As in the case of entropy, we introduce densities to transform this simple expression:

$$\frac{d}{dt}\int_{\mathcal{V}} \rho_Q dV = -\int_{\mathcal{A}} j_Q dA \tag{13.36}$$

If we use the divergence rule, we obtain the local form of the law of balance of charge:

$$\frac{\partial \rho_Q}{\partial t} + \frac{\partial j_Q}{\partial x} = 0 \qquad \textbf{(13.37)}$$

in a single spatial direction. This result is equivalent to Equ.(13.17) with $\pi_Q = 0$. As before, the law of balance of charge will be made use of in conjunction with appropriate constitutive relations. Here, I will only use those for ohmic conduction and for diffusion coupled with inductive effects.

13.4.2 Constitutive Relations for Conduction and Induction

There are constitutive relations between (1) potential and stored charge, (2) gradient of potential and current of charge, and (3) gradient of potential and rate of change of current of charge. The first is the capacitive relation of the material, the second is Ohm's law, and the third is the law of induction. The capacitive relation can be formulated as follows:

$$\dot{\rho}_Q = c''\dot{\varphi} \qquad \textbf{(13.38)}$$

where c'' is the volumetric electric capacitance of the material (capacitance per volume). This compares to Equ.(13.33), i.e., to the thermal capacitive relation between entropy and temperature of a material which is written with the specific entropy capacitance instead.

Ohmic transport and the diffusion equation. The constitutive relation for ohmic transport is equivalent to Fourier's law of the conduction of entropy, Equ.(13.18):

$$j_Q = -\sigma \frac{\partial \varphi}{\partial x} \qquad \textbf{(13.39)}$$

The relations just formulated, i.e., Equ.(13.38) and Equ.(13.39), can be introduced in the law of balance of charge, Equ.(13.37). Doing so leads to

$$c''\dot{\varphi} = \frac{\partial}{\partial x}\left(\sigma \frac{\partial \varphi}{\partial x}\right) \qquad \textbf{(13.40)}$$

which is the field equation for the electric potential equivalent to the field equation for temperature presented in Equ.(13.34). This is called a *diffusion equation*.

Inductive effects and the wave equation. Inductive effects were discussed in Chapters 1 and 3. The local form of the law of induction states that the gradient of the (inductive) electric potential leads to the rate of change of the electric current. If we use Equ.(3.41) as a guide, we see that the local form of the law of induction in electric conductors can be written as follows:

$$\frac{\partial \varphi_L}{\partial x} = -L'A\frac{\partial j_Q}{\partial t} \qquad \textbf{(13.41)}$$

where A is the cross section of the conductor and L' is the inductance per length. In a conductor having a finite conductivity, the gradient of the potential is made up of the gradients due to conduction and to induction:

$$\frac{\partial \varphi}{\partial x} = -\frac{1}{\sigma} j_Q - L' A \frac{\partial j_Q}{\partial t} \tag{13.42}$$

This is equivalent to Equ.(1.37) for the transport of a fluid. Introducing this and the expression in Equ.(13.38) into the law of balance in Equ.(13.37) yields

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{L' C'} \frac{\partial^2 \varphi}{\partial x^2} - \frac{1}{\sigma A L'} \frac{\partial \varphi}{\partial t} \tag{13.43}$$

As mentioned before in Section 3.6, this expression is called a *wave equation*. In contrast to Equ.(3.44), it contains a dissipative term due to conduction with a finite conductivity. Giving the conductivity of the material an infinitely high value, i.e., setting the resistivity equal to zero, leads to a wave equation equivalent to Equ.(3.44):

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{L' C'} \frac{\partial^2 \varphi}{\partial x^2} \tag{13.44}$$

13.4.3 The Speed of Propagation of Electrical Pulses

The wave equation for undamped transports as in Equ.(13.44) admits a simple general solution for travelling waves. Consider the function $\varphi(0,x)$ shown as a solid line in Fig. 13.2. If it travels to the right at speed c without changing its shape, we can say that

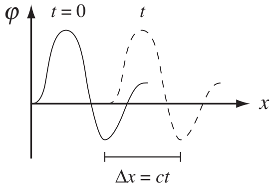


Figure 13.2: A wave travelling to the right at speed c.

$$\varphi(t,x) = \varphi(t, x - ct) \tag{13.45}$$

This can be introduced in Equ.(13.44) which leads to

$$c^2 \frac{\partial^2}{\partial t^2} \varphi(t, x - ct) = \frac{1}{L' C'} \frac{\partial^2}{\partial x^2} \varphi(t, x - ct)$$

Comparison with the original equation Equ.(13.44) shows that the speed of propagation c is related to the inductance per length and the capacitance per length of the conductor by

$$c^2 = \frac{1}{L' C'} \tag{13.46}$$

Now consider *pure conduction* of charge. Obviously, the difference between this and the situation that leads to the wave equation Equ.(13.43) has to be found in the constitutive law of Equ.(13.42) which includes the effect of induction. Without induction we have $L' = 0$. Using this condition in Equ.(13.43) leads to

$$\frac{C'}{A} \frac{\partial \varphi}{\partial t} = \sigma \frac{\partial^2 \varphi}{\partial x^2} \tag{13.47}$$

Since Equ.(13.47) requires $L' = 0$, this also means that the speed of propagation of an electrical pulse must be infinitely high in pure conduction. Clearly, this is an unrealistic result which shows that the classical theory of conduction has its shortcomings. We can defend its use by noticing that the model yields useful results in the case of very small inductance. This condition is met in many electrical, chemical, and thermal phenomena.

13.5 INDUCTIVE THERMAL BEHAVIOR

Irrespective of the material undergoing thermal processes, all the examples discussed so far have led to the same basic result concerning the functional dependence of entropy and energy. We have found that even in irreversible processes the local behavior of materials is the same as that encountered in the simplest of all cases, namely, in static conditions or in the dynamics of uniform ideal fluids. The entropy and the energy of a simple material have always been found to depend only upon temperature and density. We have discovered the same type of Gibbs Fundamental Form in each example. Because of this similarity, we speak of local thermodynamic equilibrium prevailing even in the case of irreversible processes such as those treated for heat-conducting viscous fluids.

Despite the success of the models of materials treated so far, in at least one case it has been known for a long time that something is amiss: the simple theory of conduction of heat based upon Fourier's law predicts infinite speed of propagation of thermal disturbances. This we can conclude by analogy with the case of pure electric conduction treated in Section 13.4.3.

We do not have to advance theories of more complicated materials to find the need to extend the usual results of thermodynamics. We will see in this section that pure conduction of heat calls for a treatment where the energy and the entropy of a body are functions of *nonequilibrium variables* in addition to local temperature and density, if we wish to solve the problem of infinite speed of propagation of thermal pulses. A simple derivation of the consequences for thermodynamics of the additional assumption will be given for the case of conduction in a rigid conductor of constant density.

13.5.1 Classical Theory of the Speed of Thermal Transports

Normal conduction of heat through a rigid conductor is described by the laws of balance of entropy and energy for constant density of the conductor:

$$\begin{aligned} \rho\dot{s} + \frac{\partial}{\partial x} j_S &= \pi_S \\ \rho\dot{e} + \frac{\partial}{\partial x} j_{E,th} &= 0 \end{aligned} \tag{13.48}$$

by Fourier's law of conduction

$$j_S = -k_S \frac{\partial T}{\partial x} \tag{13.49}$$

and by the relation between energy currents and entropy currents:

$$j_{E,th} = T\, j_S \tag{13.50}$$

s and *e* are the specific entropy and specific energy of the materials, respectively. Consequences of this are the expression for the rate of production of entropy

$$\pi_S = -\frac{1}{T} j_S \frac{\partial T}{\partial x} \tag{13.51}$$

and the simple Gibbs Fundamental Form

$$\dot{e} = T\,\dot{s} \tag{13.52}$$

This means that the entropy and the energy of the body are functions of temperature only. Furthermore, as derived in Section 13.3, the field equation for temperature in a rigid conductor is

$$\rho c \frac{\partial T}{\partial t} = k_E \frac{\partial^2 T}{\partial x^2} \tag{13.53}$$

which follows from Equ.(13.34) for constant values of the conductivity with respect to energy. The field equation should be compared to Equ.(13.47) for the conduction of charge. Clearly, the two are equivalent. The equation representing conduction alone is obtained from more general laws if induction is neglected. Doing so means setting the inductance equal to zero, which, in turn, means that the speed of propagation of the waves approaches infinity, Equ.(13.46). In other words, the classical theory of conduction predicts infinite speed for thermal pulses. This is a totally unphysical result; a resolution of this problem will now be presented.

13.5.2 Thermal Inertia

If we assume a current of entropy to have some type of “inertia” associated with it, we should simply include a thermal inductance with the law of conduction of heat, i.e., with Fourier’s law, which then becomes

$$\tau_S \frac{\partial j_S}{\partial t} + j_S = -k_S \frac{\partial T}{\partial x} \tag{13.54}$$

where τ_S, the relaxation time of the current of entropy, is equal to the ratio of thermal inductance to thermal resistance; i.e., it is equivalent to the inductive time constant known from electricity or from hydraulics. Equ.(13.54) is known as the law of Maxwell-Cattaneo for the conduction of heat (which is commonly formulated for the flow of energy). Combined with the law of balance of energy in pure heat conduction, this leads to a hyperbolic partial differential equation for the temperature, i.e., to a wave equation (telegrapher’s equation) for the conduction of entropy. As we have seen before, such a field equation means that thermal disturbances propagate with finite speed, which in this case is given by

$$v = \sqrt{\frac{k_S}{\tau_S \rho \kappa}} \tag{13.55}$$

Here, *c* and ρ are the specific temperature coefficient of energy and the density of the material, respectively. Zero relaxation time for currents of heat, i.e., immediate reaction to changes of temperature gradients, therefore leads to infinite speed of propagation as predicted by Fourier's law of conduction of heat. Phenomena which predict finite speed disturbances in thermal processes are known to exist in high-frequency processes where frequencies become comparable to the inverse of the inductive time constant (ultrasonic propagation in gases, neutron scattering in liquids), or in solids at very low temperatures (second sound).

A qualitative explanation of inductive phenomena usually involves the notion of the energy associated with the processes. In electrodynamics, the energy of the magnetic field is increased or decreased in accordance with the change of the magnitude of the currents of charge. In hydraulics, on the other hand, the energy change of the flowing fluid, i.e., its kinetic energy, is associated with changes of currents. At first, we might look in vain for the energy related to the "inertia" of currents of entropy. However, the energy flowing together with entropy represents a flux of mass: energy has inertia. Changing the currents of entropy leads to a change of the associated flux of energy (mass), which should provide the effect we have been looking for.

13.5.3 Conduction Including Inductive Effects

It will be shown now that we should include the flux of entropy as one of the independent variables of a theory of conduction if we wish to account for phenomena which predict finite speed of propagation of heat.[2] Having equations like those presented in the previous section calls for evolution equations not only for the entropy (and the energy), but for their currents as well. Therefore, let us assume a Gibbs Fundamental Relation of the form

$$\dot{e} = T\,\dot{s} + a\,j_S\,\frac{dj_S}{dt} \tag{13.56}$$

which implies

$$s = s(T, j_S) \tag{13.57}$$

and

$$e = e(T, j_S) \tag{13.58}$$

The equations of balance of entropy and of energy, i.e., Equ.(13.48), remain unchanged. If we plug the Gibbs relation into the law of balance of energy, we obtain

$$\rho\left(T\,\dot{s} + a\,j_S\,\frac{dj_S}{dt}\right) + \frac{\partial}{\partial x}\,j_{E,th} = 0$$

which is equivalent to

$$\rho T\,\dot{s} + T\,\frac{\partial}{\partial x}\left(\frac{j_{E,th}}{T}\right) = -\rho a\,j_S\,\frac{dj_S}{dt} - \frac{1}{T}\,j_{E,th}\,\frac{\partial T}{\partial x}$$

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[2] The treatment given here is a variation on the theme presented in a paper by Jou and Casas-Vázquez (1988). I am discussing the phenomenon using entropy rather than energy.

Now compare this result to the equation of balance of entropy. We obtain the following expressions for the flux of energy in terms of the flux of entropy, and for the rate of production of entropy:

$$j_S = \frac{j_{E,th}}{T} \tag{13.59}$$

$$\pi_S = \frac{1}{T}\left(-\rho a \frac{dj_S}{dt} - \frac{\partial T}{\partial x}\right) j_S \tag{13.60}$$

Note that we again have the well-known relation between currents of entropy and energy in conduction. The entropy production rate is different from Equ.(13.51), however. Now we exploit the fact that the entropy production may not be negative. The simplest possibility for this to be the case is if

$$-\rho a \frac{dj_S}{dt} - \frac{\partial T}{\partial x} = b\, j_S \quad \text{with} \quad b > 0$$

Comparison with the constitutive law assumed to hold for the current of energy, i.e., with the law of Maxwell-Cattaneo (13.54) allows us to identify the coefficients *a* and *b* used in the previous relations:

$$b = \frac{1}{k_S}$$

$$a = \frac{\tau_S}{\rho k_S}$$

Therefore, the rate of production of entropy turns out to be

$$\pi_S = -\frac{1}{T}\left(\frac{\tau_S}{k_S} \frac{dj_S}{dt} + \frac{\partial T}{\partial x}\right) j_S \tag{13.61}$$

while the Gibbs Fundamental Form is given by

$$\dot{e} = T\,\dot{s} + \frac{\tau_S}{\rho k_S}\, j_S \frac{dj_S}{dt} \tag{13.62}$$

Naturally, for vanishing relaxation time τ_S (or for vanishing time rates of change of fluxes) the results are equivalent to the usual case of heat conduction according to Fourier's law. It is obvious that the requirement of finite speed of propagation of thermal disturbances requires the fluxes to be included in the list of the independent variables of the theory. The resulting entropy and energy of a body are called *nonequilibrium entropy* and *energy*; in addition to terms which depend only upon temperature and density, i.e., upon the equilibrium conditions, they include a term involving the square of the entropy flux.[3] This requirement distinguishes the extended version of irreversible thermodynamics from the usual one.

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[3] See Jou and Casas-Vázquez (1988), p.332.

QUESTIONS

9. Dynamical models of thermal processes can be produced for simple materials which admit so-called equilibrium relations. What is the meaning of this? What then is the meaning of non-equilibrium relations?
10. Explain Equ.(13.54) in terms of the power of thermal processes.
11. Why should the expression in parentheses in Equ.(13.60) be made proportional to the current of entropy?

13.6 THERMOELECTRICITY

Thermoelectric devices were first discussed in Section 4.7.2 from the viewpoint of spatially uniform systems. Now, we are going to develop the description of thermoelectricity based upon spatially continuous models.[4] Apart from the typical approach that uses entropy as the fundamental thermal quantity, this section will demonstrate a simplified derivation of the relation between the Seebeck coefficient and the Peltier factor. It is based upon the same continuum physics model which is used to present the theory of thermoelectricity.

Applications of thermoelectricity have met with increased interest in recent years. Thermoelectric power generation in space or cooling of electronic devices are just two of many examples. The fact that temperatures at the surfaces of Peltier devices can be controlled easily and quickly has led to applications in biology and medicine.[5]

13.6.1 Observations

There are two observations which allow us to create a formal description of the thermoelectric effect. First, if a temperature gradient is established through a thermoelectric device, we can measure a gradient of the electric potential. Second, if electricity is made to flow through a device, entropy is forced to flow along with charge.

Thermoelectric coefficients. The Seebeck coefficient ε and the Peltier factor α are introduced as follows. The former establishes the relation between the temperature gradient and the gradient of the electrochemical potential μ_{ec} if no electric current is allowed to flow through the thermoelectric device:

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[4] Discussions of important aspects of thermoelectricity can be found in W. C. Scott (1962): "Electron Levels, Electrochemical Effects, and Thermoelectricity," Am. J. Phys. **30**, 727-737; P. L. Walstrom (1988): "Spatial dependence of thermoelectric voltages and reversible heats," Am. J. Phys. **56**, 890-894; J. M. Gordon (1991): "Generalized power versus efficiency characteristics of heat engines: The thermoelectric generator as an instructive illustration," Am. J. Phys. **59**, 551-555; Chen et al. (2007): "Irreversible transfer processes of thermoelectric generators," Am. J. Phys. **75**, 815-820. See also references therein.

[5] D. A. Van Baak (1992): "Temperature servomechanisms using thermoelectric modules," Am. J. Phys. **60**, 803-815; G. Reid et al. (2001): "A system for applying rapid warming or cooling stimuli to cells during patch clamp recording or ion imaging," Journal of Neuroscience Methods **111**, 1–8; S. M. Rothman et al. (2005): "Focal cooling for epilepsy," Epilepsy & Behavior **7**, 214–221.

$$\nabla\mu_{ec} = -\varepsilon\nabla T \tag{13.63}$$

∇ is the symbol for the multidimensional gradient. This is the formal expression of our knowledge gained from the use of thermocouples. A temperature difference of 1 K leads to an electro-chemical potential difference of ε volts.

μ_{ec} is the electro-chemical potential (of the charge carriers in the material) per charge of one mole of charge carriers, i.e., it is the standard electro-chemical potential divided by the Faraday constant (see Chapter 6). If concentration differences and the temperature dependence of the chemical part of the potential can be neglected, μ_{ec} equals the electric potential (measured in volts). This is the case for a voltmeter used to measure the voltage across a thermoelectric device.[6]

The Peltier coefficient α is the factor that determines the coupling between currents of charge and of entropy.[7] It is observed that, even for isothermal conditions, entropy is transported through a thermoelectric cooling device (Peltier device) if an electric current j_Q is made to flow through it. This observation is summarized as follows:

$$\mathbf{j}_S = \alpha\,\mathbf{j}_Q \tag{13.64}$$

j denotes a current density vector. Expressed graphically, an electric current sweeps α units of an entropy current along with it when there is no temperature difference. Note that the entropy flow in Equ.(13.64) is expected to be non-dissipative in contrast to conduction of entropy that is caused by a temperature gradient.

13.6.2 Assumptions

We base our reasoning on the standard form of the laws used to model thermal and electric processes. These are (1) the laws of balance of entropy and of charge (or of number of particles of the charge carrier); (2) the law of balance of energy supplemented by the expression for the total energy current in terms of the flows of entropy and charge. Constitutive laws for the flows of charge and entropy suggested by experiments, as discussed above, will be described in Section 13.6.3.

We shall write the equations for the purely one-dimensional case with flows only in the axial direction of a rod made of a conducting material. Furthermore, we shall treat the steady-state case.

Balance of entropy and charge. The thermoelectric effect is the result of the coupled flow of entropy and charge in a conducting material. Therefore, we shall make use of the steady-state forms of the laws of balance of entropy:

$$\frac{dj_S}{dx} = \pi_S \tag{13.65}$$

and of charge:

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[6] For details see P. L. Walstrom (1988).

[7] In traditional texts, the factor $T\alpha$ is commonly called the *Peltier coefficient*. See for example, Zemansky and Dittman (1981), p. 338.

$$\frac{dj_Q}{dx} = 0 \tag{13.66}$$

x denotes the single independent spatial variable. See the Sections 13.1 - 13.4 for more details concerning these laws of balance. Note that possible sources of entropy have not been included.

Energy. The steady-state law of balance of energy is very simple: the divergence of the total energy flux density must be equal to zero:

$$\frac{dj_E}{dx} = 0 \tag{13.67}$$

The total energy current j_E can be split into two terms, each arising from the transport of one of the basic quantities (i.e., entropy and charge):

$$j_E = T\,j_S + \mu_{ec}\,j_Q \tag{13.68}$$

This follows directly from our image of entropy and charge as energy carriers.

13.6.3 Constitutive Laws

There is one constitutive law for each of the flux densities of charge and of entropy. If we allow for an electric current through a thermoelectric generator, Equ.(13.63) is generalized to:

$$j_Q = -\sigma\frac{d\mu_{ec}}{dx} - \sigma\varepsilon\frac{dT}{dx} \tag{13.69}$$

σ is the electric conductivity of the material. If we combine the two terms on the right hand side, we see that there is a combined thermo-electro-chemical potential (i.e., $\mu_{tec} = \mu_{ec} + \varepsilon T$) that gives rise to the electric current:

$$j_Q = -\sigma\frac{d}{dx}\left(\mu_{ec} + \varepsilon T\right) = -\sigma\frac{d}{dx}\mu_{tec} \tag{13.70}$$

The second constitutive relation is a generalization of Equ.(13.64). Allowing for a temperature gradient we have:

$$j_S = \alpha\,j_Q - k_S\frac{dT}{dx} \tag{13.71}$$

Here, k_S is the entropy conductivity of the material. Equ.(13.71) suggests that the entropy current consists of a non-dissipative and a dissipative term. If Equ.(13.69) is inserted into Equ.(13.71), the two laws may be summarized as follows:

$$\begin{aligned} j_Q &= -\sigma\frac{d\mu_{ec}}{dx} - \sigma\varepsilon\frac{dT}{dx} \\ j_S &= -\sigma\alpha\frac{d\mu_{ec}}{dx} - \left(\sigma\alpha\varepsilon + k_S\right)\frac{dT}{dx} \end{aligned} \tag{13.72}$$

Onsager's relations assert that the matrix of coefficients multiplying the gradients is symmetric. In our case, this means that we should expect the following relation to hold:

$$\alpha = \varepsilon \tag{13.73}$$

This will be demonstrate in the following sections.

13.6.4 Entropy Production

As stated above, we shall gain additional information on the material coefficients of the theory, i.e., the Seebeck coefficient and the Peltier factor, by considering the form of the terms in the equation for the entropy production rate and for the power of the thermoelectric process (for the latter, see Section 13.6.5).

We begin with the law of balance of energy in Equ.(13.67) and insert Equ.(13.68). Taking into account the laws of balance of entropy and charge, the density of the entropy production rate is obtained:

$$T\,\pi_S = -j_S \frac{dT}{dx} - j_Q \frac{d\mu_{ec}}{dx} \tag{13.74}$$

The two terms on the right hand side represent the thermal and the electric power of the processes, respectively. Since these contain non-dissipative parts, only the sum of the two terms can be equal to the entropy production rate. By itself, a single term does not represent a part of the entropy production rate. If we insert the constitutive laws of Equ.(13.69) and Equ.(13.71), we see that

$$T\,\pi_S = -\alpha\, j_Q \frac{dT}{dx} + k_S \left(\frac{dT}{dx}\right)^2 + \frac{1}{\sigma} j_Q^2 + \varepsilon\, j_Q \frac{dT}{dx} \tag{13.75}$$

The first and the last of the terms are non-dissipative parts of the thermal and the electric power, respectively. Since they do not add to the production of entropy, their sum must cancel in Equ.(13.75). This leads immediately to $\alpha = \varepsilon$ (Equ.(13.73)) and to

$$\pi_S = \frac{1}{T} k_S \left(\frac{dT}{dx}\right)^2 + \frac{1}{T}\frac{1}{\sigma} j_Q^2 \tag{13.76}$$

This is what we should have expected from our knowledge of dissipation due to the conduction of entropy and of charge.

13.6.5 Power of thermoelectric processes

Since the phenomena of thermoelectric power generation and of Peltier cooling are assumed to be caused by the same underlying effect, we should expect a relation to exist between the Seebeck coefficient and the Peltier factor. In fact, as we know, they are equal. This can be shown to be a consequence of the dependence of the entropy production and the power upon fluxes, gradients, and material factors such as α and ε.

Take the case of thermoelectric power generation. A current of entropy is established as a consequence of a temperature difference. This leads to an electric and two dissipative processes. The density of the power of the driving thermal process p_{th} is equal to

$$p_{th} = -j_S \frac{dT}{dx} \tag{13.77}$$

which can be expressed with the help of Equ.(13.69) and Equ.(13.71):

$$p_{th} = \frac{\alpha}{\sigma\varepsilon} j_Q^2 + \frac{\alpha}{\varepsilon} j_Q \frac{d\mu_{ec}}{dx} + k_S \left(\frac{dT}{dx} \right)^2 \tag{13.78}$$

In this expression, we can interpret all three terms on the right hand side. The third is the dissipation rate as a consequence of thermal conduction. The first must represent the dissipation rate due to charge conduction, whereas the second determines the non-dissipative power of the electric process driven by a part of the input power.[8] The sum of the three terms must obviously equal the total power of the thermoelectric process. Again, these identifications lead us to conclude that the Seebeck coefficient and the Peltier factor should be equal.

13.6.6 Thermo-electric potential and electro-thermal transport

The results of the previous two sections rest upon the differentiation between irreversible and non-dissipative parts of the thermoelectric effect. They may be summarized in the following graphical interpretation of this phenomenon.

1. The transports of charge and of entropy are coupled according to Equ.(13.64). This leads to a non-dissipative part of the total entropy current (the dissipative part is due to conduction):

$$j_S = j_{S,cond} + j_{S,TE} = j_{S,cond} + \alpha j_Q \tag{13.79}$$

2. It is this coupling, i.e., the non-dissipative entropy transport, which leads to the thermo-electric potential (or rather, to its gradient):

$$\frac{d\mu_{TE}}{dx} = -\varepsilon \frac{dT}{dx} \tag{13.80}$$

The assertion that 2 follows from 1 is equivalent to saying that the energy released as a consequence of the non-dissipative entropy transport is equal to the energy made available to the thermoelectric process:

$$j_{S,TE} \frac{dT}{dx} + j_Q \frac{d\mu_{TE}}{dx} = 0 \tag{13.81}$$

Once more, this results in the equality of the Seebeck coefficient and the Peltier factor. The steps and the reasoning presented here may be taken as a simple description of thermoelectricity.

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[8] Integration of the second term for the thermoelectric generator shows that this term is indeed equal to the rate at which energy is made available to the user of the device, if we set $\varepsilon = \alpha$. See also Walstrom (1988).

13.6.7 Summary

If we accept some strong physical reasoning with regard to the nature of the dissipative processes inherent in thermoelectricity, we can apply the same equations used to model the phenomena to demonstrate the equality of the Seebeck coefficient and the Peltier factor.

The argument starts with the assumption that the only irreversibilities are the result of conduction of entropy and charge. As a consequence, we reason that the coupling of entropy currents to currents of electric charge causes a non-conductive flow of entropy (Equ.(13.64) and Equ.(13.79)) which is non-dissipative; it leads to the reversible effect of a thermoelectric device. Since we know the expressions for the irreversibilities due to the conduction of charge and entropy, we have prior knowledge of the form of the entropy production rate: it should be as presented in Equ.(13.76). This immediately leads to the desired result.

Should we accept such reasoning? There are compelling reasons for doing this. The alternative would be to appeal to the Onsager relations. Simply appealing to someone's result without the accompanying proof is probably worth less to the learner than reasoning based on assumptions that can be motivated and whose consequences can be inspected. Moreover, the derivation of Onsager's reciprocity relations suffers from limitations. Therefore, they are usually taken for granted at the macroscopic level. A general proof in macroscopic physics is still missing.[9]

QUESTIONS

12. What kind of experiment could be used to justify Equ.(13.64)?
13. Why should we use the electro-chemical potential rather than the pure electric potential when we formulate thermo-electric phenomena?
14. What is the meaning of the thermo-electro-chemical potential?
15. When discussing Equ.(13.71), it was stated that there are two different entropy transports. What do these transports represent?
16. Consider thermoelectric cooling. What are the origins of the entropy transports occurring in a Peltier device? What is the condition that cooling actually takes place?
17. In what sense is Equ.(13.76) self-evident?
18. Why do the first and last terms on the right hand side of Equ.(13.75) represent non-dissipative processes? Why does this mean that they do not contribute to entropy production?

EXERCISES AND PROBLEMS

1. The ends of a copper cylinder length 0.50 m and diameter 0.05 m have constant temperatures of 373 K and 273 K. Entropy is conducted in the direction of the axis of the cylinder only. The thermal conductivity with respect to energy of copper is 384 W/(K·m), which we assume to be constant. Calculate (a) the energy current density, (b) the energy flux, and

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[9] For a proof in a special case, see I. Müller, *Thermodynamics* (Pitman, Boston, 1985), p. 203-208.

(c) the production densities of entropy at the ends of the cylinder. (d) From the production density as a function of position determine the production rate of entropy in the copper bar. Show that the result is equal to the net current of entropy.

2. Derive the field equation for temperature in steady-state conduction on the basis of the balance of energy instead of the balance of entropy.

3. According to Table 7.1, the conductivity with respect to entropy of water depends less upon temperature than its counterpart, the conductivity with respect to energy. Taking the former quantity as constant for steady-state conduction through a slab of water (a) should the temperature gradient be steeper at the hotter or at the cooler side? (b) Show that the field equation for temperature should take the form

$$T\frac{d^2T}{dx^2}+\left(\frac{dT}{dx}\right)^2=0$$

4. Calculate (a) the source density of energy and (b) the production (or source) density of entropy in a 1-kg sample of enriched uranium at a temperature 300 K. Uranium has a density of 18950 kg/m^3. Assume there to be 97% U-238 and 3% U-235. The energy released in the decay of one nucleus is roughly 4.2 MeV and 4.6 MeV, respectively. The half-lives of the two isotopes are $4.5\cdot 10^9$ years and $7.1\cdot 10^8$ years, respectively.

5. Consider the conduction of heat through the Earth's crust, whose geometry can be taken as flat. Allow for sources of entropy in the material which are assumed to be distributed evenly, and let the conductivity with respect to energy be constant. (a) Show that the temperature profile from the base of the crust to the surface is

$$T(x)=T_L+\frac{1}{2}\frac{\sigma_E}{k_E}\left(L^2-x^2\right)+\frac{1}{k_E}j_E(0)(L-x)$$

for a given energy flux $j_E(0)$ at the base and surface temperature T_L. (The thickness of the crust is L.) (b) Determine the dependence of the temperature gradient near the surface upon the conductivity, the energy flow at the base, and the source rate of energy in the material. (c) Calculate the surface temperature gradient for a thickness of the crust of 50 km, a thermal conductivity of 2.5 W/(K·m), and a source rate of $1.25\cdot 10^{-6}$ W/m^3.

6. Repeat the calculation of the steady-state temperature profile in a slab of matter such as the Earth's crust (Problem 5), but this time for a source rate of energy which decreases exponentially from the surface. Again, boundary conditions are given at the bottom (the energy flux is fixed) and at the top (the temperature is specified).

7. Show that for pure conduction, with sources of heat in the material, the field equation for temperature must take the form

$$\frac{\partial T}{\partial t}=\frac{k_E}{\rho c}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right)+\frac{\sigma_E}{\rho c}$$

in radial symmetry if non-steady-state conditions are considered.

8. Show that the following holds for the density of the entropy production rate

$$\pi_S=\frac{1}{T}\frac{1}{k_S}j_S^2$$

both for conduction with and without inductive effects. Why is the form derived in Equ.(13.61) different from the simpler for classical conduction, i.e., from Equ.(13.51)? How does this difference arise?

9. Show that the field equation for temperature in a single-dimensional thermoelectric device operated dynamically is given by

$$\frac{\rho c}{k_E}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{j_Q^2 \rho_{el}}{k_E}$$

Here, ρ_{el} is the electric resistivity, and ρ and c are the density and the specific heat of the material, respectively. k_E symbolizes the thermal (energy) conductivity. (a) What are the assumptions concerning material properties of the device? (b) Use qualitative reasoning to justify the equation by identifying the meaning of its parts. (c) Provide a formal derivation based on the equations formulated in Section 13.6.2 and Section 13.6.3.

10. Consider a thermoelectric device (as in Problem 9) operated as a cooler. To study the behavior of the cold end under fast transient operation, formulate boundary conditions for the following case: the cold end of the device is thermally insulated, the hot end is kept at a steady temperature.

11. The thermal energy currents at the hot and cold ends of thermoelectric generators are commonly written as follows:

$$I_{E,th,h} = \alpha I_Q T_h + G_E\left(T_h - T_c\right) - \frac{1}{2} R I_Q^2$$
$$I_{E,th,c} = \alpha I_Q T_c + G_E\left(T_h - T_c\right) + \frac{1}{2} R I_Q^2$$

h and c stand for hot and cold, respectively. (a) What are the assumptions regarding the (energy) conductance G_E. (b) Derive these expressions from what you know about the conduction of heat. Show that the terms $\pm R I_Q{}^2/2$ are a consequence of the special assumptions made here. (c) Use the expressions to derive the power and the efficiency of the generator.

12. While the steps that lead from Equ.(13.75) to Equ.(13.76) may be convincing on physical grounds, they are not necessary for purely mathematical reasons. For the entropy production rate in Equ.(13.75) to be strictly non-negative, we only require the following conditions: $k_S \geq 0$, $\sigma \geq 0$, and $4k_S/\sigma \geq (\varepsilon - \alpha)^2$. Prove this statement.

CHAPTER 14

CONVECTIVE HEAT TRANSFER

Convective transport of heat leads to many interesting natural phenomena and to important technical applications. Theoretically, the subject is very demanding. For this reason we have so far dealt with convection only briefly. In Chapter 7, we used a simple expression to calculate heat transfer at a solid-fluid interface. Knowing the heat transfer coefficient, we can establish a relation which serves as a boundary condition for processes inside a particular body. Uniform flow systems were discussed in Chapter 8, which led to expressions for entropy and energy transported by a fluid.

Here we will take a second step by also considering the effect of convection at surfaces upon the fluid carrying away, or delivering, entropy. If we still assume the heat transfer coefficients at interfaces to be given, and if we treat simple fluid flow as in Chapter 8, we can calculate the performance of devices such as solar collectors and heat exchangers. In addition to these technical applications, convective heat transfer in an atmosphere (or inside a star) will be discussed.

14.1 THEORY OF CONVECTIVE HEAT TRANSFER

It should be obvious that the fundamental problem of how to calculate heat transfer coefficients has still not been solved. While we have derived more or less general results for the Navier-Stokes-Fourier fluid in Chapter 11, the present section will demonstrate how the equations can be specialized to apply to a simple case of boundary layer flow. Convective heat transfer at a solid-fluid interface leads to this type of flow; by looking at the proper laws of balance and constitutive relations, we will get a first encounter with how heat transfer coefficients can be calculated.

The application to be treated here will first require a generalization of the equations to the two-dimensional case. Second, we will apply a number of special assumptions that hold for steady laminar and incompressible boundary layer flow, which will lead to a considerable reduction of complexity of the equations. Finally, we will see how the relations can be applied to the problem of forced flow over a flat plate.

14.1.1 The Boundary Layer

We first encountered the problem of heat transfer at a solid-fluid interface in Section 7.3, where the boundary layer developing at the surface of a solid body was briefly described. Here, some remarks will be added to the previous treatment.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_15,

The boundary layer is the region near a surface in which the conditions of the fluid change from those at the surface to those in the free stream. All the interesting action takes place in this normally very thin layer. Naturally, there is no sharp line dividing the boundary layer from the undisturbed fluid. Therefore, it is common to specify that, say, 99% of the change of velocity and temperature perpendicular to the surface will occur between the surface and the line depicting the "edge" of the boundary layer in Fig. 14.1. Note that the change of temperature and of velocity do not have to take place over the same normal distance, which means that the thermal boundary layer and the velocity boundary layer do not have to have the same thickness (these thicknesses are denoted by δ_t and δ, respectively). It is clear that to solve a convective heat transfer problem, we will have to determine the temperature and velocity profiles over the range of the surface.

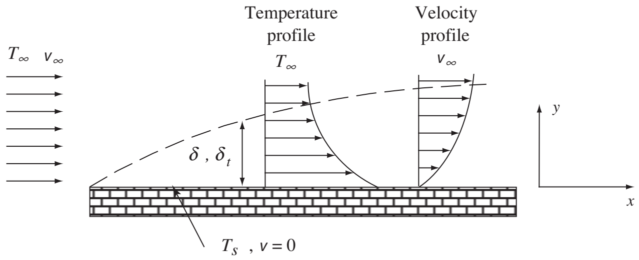

Figure 14.1: Boundary layer flow was discussed briefly in Chapter 7, Section 7.3. Temperature and speed vary in a thin layer from their values at the interface to the free stream values of the fluid. If the geometrical arrangement extends far in the direction perpendicular to the drawing, we basically can treat the flow as two-dimensional.

From the discussion in Chapter 7 (see, in particular, Section 7.3.2) we can infer what it takes to determine the heat transfer coefficient with respect to energy. There, we found that this quantity can be calculated as follows:

$$h = -\frac{k_{Ef}}{T_s - T_\infty} \left. \frac{\partial T}{\partial y} \right|_{y=0} \tag{14.1}$$

Here, h is the heat transfer coefficient used to calculate the energy flux associated with the conductive flux of entropy at the interface; k_{Ef} is the thermal conductivity of the fluid. Obviously, in addition to fluid properties, we need to know the temperature gradient at the surface, which in turn depends upon the conditions in the boundary layer.

Since the velocity and the thermal boundary layers are related, we need to know the mechanical conditions as well. Indeed, we may say that the entire problem starts with the effect of friction at the surface over which the fluid is flowing. To specify this phenomenon, we introduce a dimensionless friction coefficient which is defined as the ratio of the shear stress at the surface and the density of kinetic energy of the fluid in the free stream:

$$C_f = \frac{-j_{pxy}(y = 0)}{\rho v_\infty / 2} \tag{14.2}$$

Introduction of Newton's law of friction (see Section 3.2.3 and Chapter 11) yields

$$C_f = \frac{\mu}{\rho v_\infty / 2} \left. \frac{\partial v_x}{\partial y} \right|_{y=0} \tag{14.3}$$

Therefore, the conditions in the velocity boundary layer determine the friction coefficient, or vice versa. Again, knowing the conditions of the fluid at the interface is of central importance in calculating the outcome of convective heat transfer.

14.1.2 The General Equations for Two Dimensional Flow

The laws of balance and the constitutive relations were listed for the general case of three-dimensional flow in Section 11.8. The only difference between the two- and the three-dimensional cases is to be found in the indices *i* and *j*, which for the present case, extend only from 1 to 2. Taking into consideration the results of the thermodynamic constitutive theory presented there, the laws of balance are

$$\begin{aligned}
&\frac{D\rho}{Dt}+\rho\frac{\partial v_j}{\partial x_j}=0\\
&\rho\frac{Dv_i}{Dt}+\frac{\partial j_{pij}{}^{(c)}}{\partial x_j}=0\\
&\rho\frac{Du}{Dt}+j_{pij}{}^{(c)}d_{ij}+\frac{\partial j_{E,th,j}}{\partial x_j}=0
\end{aligned} \tag{14.4}$$

if they are written in the material form.[1] It is customary to leave out the law of balance of entropy, and include the results of the constitutive theory of the thermal processes with the energy equation. The material derivative and the symmetric part of the velocity gradient tensor are given by

$$\frac{D}{Dt}=\frac{\partial}{\partial t}+v_j\frac{\partial}{\partial x_j} \tag{14.5}$$

$$d_{ij}=\frac{1}{2}\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}\right) \tag{14.6}$$

For our purpose, *i,j* = 1,2. The constitutive laws pertaining to the Navier-Stokes-Fourier fluid are

$$\begin{aligned}
&u=u(\rho,T)\\
&j_{pij}{}^{(c)}=P\delta_{ij}-\nu d_{kk}\delta_{ij}-2\mu d_{ij}\\
&j_{E,th}=-k_E\frac{\partial T}{\partial x}
\end{aligned} \tag{14.7}$$

The laws relating to entropy are included, for example, in the expression for the thermal energy current. (You can start with Fourier's law for conduction of entropy, use the relation between fluxes of entropy and of energy derived for the Navier-Stokes-Fourier fluid, and arrive at Equ.$(14.7)_3$.)

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[1] See Malvern (1969), p. 206–230, for a derivation of the laws of balance in the form given here. They are motivated by the one-dimensional case treated in the previous sections. As before, it is assumed that a summation is performed over indices appearing twice in a term.

14.1.3 The Navier-Stokes Equations for Steady Laminar and Incompressible Flow in Two Dimensions

As suggested by Fig. 14.1, we can treat our example as a case of two-dimensional flow. If we assume the flow to be developed, we no longer take changes in time into account. Also, with the exception of high speed flow of gases, fluids can normally be considered to be nearly incompressible.

Mass and momentum equations. Now, we will write out the equations of balance for mass and for the x- and the y-components of momentum, introduce the constitutive laws, and apply the restrictions:

$$\begin{aligned}
&\frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}=0\\
&\rho v_x\frac{\partial v_x}{\partial x}+\rho v_y\frac{\partial v_x}{\partial y}+\frac{\partial P}{\partial x}-\mu\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_x}{\partial y^2}\right)=0\\
&\rho v_x\frac{\partial v_y}{\partial x}+\rho v_y\frac{\partial v_y}{\partial y}+\frac{\partial P}{\partial y}-\mu\left(\frac{\partial^2 v_y}{\partial x^2}+\frac{\partial^2 v_y}{\partial y^2}\right)=0
\end{aligned} \tag{14.8}$$

The derivation for the case of the balance of mass is quite simple. Since the density is taken to be constant (both in space and in time), Equ.(14.4)$_1$ takes the form

$$\frac{\partial \rho}{\partial t}+v_x\frac{\partial \rho}{\partial x}+v_y\frac{\partial \rho}{\partial y}+\rho\left(\frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}\right)=0 \quad\Rightarrow\quad \frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}=0$$

There are two momentum balance equations. We shall perform the derivation for the x-component only. First, because of steady-state conditions, we have

$$\rho\left(v_x\frac{\partial v_x}{\partial x}+v_y\frac{\partial v_x}{\partial y}\right)+\frac{\partial j_{pxx}^{(c)}}{\partial x}+\frac{\partial j_{pxy}^{(c)}}{\partial y}=0$$

The constitutive law for the momentum current density is given by

$$j_{pij}^{(c)}=P\delta_{ij}-\lambda d_{kk}\delta_{ij}-2\mu d_{ij}$$

Because of the particular form of the balance of mass for the present case, the second term on the right-hand side is zero:

$$d_{kk}=\frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}=0$$

which means that

$$\begin{aligned}
j_{pxx}^{(c)}&=P-2\mu\frac{\partial v_x}{\partial x}\\
j_{pxy}^{(c)}&=-\mu\left(\frac{\partial v_x}{\partial y}+\frac{\partial v_y}{\partial x}\right)
\end{aligned}$$

The sum of the two spatial derivatives of the momentum current density vector is equal to

$$\begin{aligned}\frac{\partial j_{pxx}{}^{(c)}}{\partial x}+\frac{\partial j_{pxy}{}^{(c)}}{\partial y}&=\frac{\partial P}{\partial x}-\left\{\frac{\partial}{\partial x}\left[2\mu\frac{\partial v_x}{\partial x}\right]+\frac{\partial}{\partial y}\left[\mu\left(\frac{\partial v_x}{\partial y}+\frac{\partial v_y}{\partial x}\right)\right]\right\}\\ &=\frac{\partial P}{\partial x}-\left\{\mu\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_x}{\partial y^2}\right)+\mu\left(\frac{\partial}{\partial x}\frac{\partial v_x}{\partial x}+\frac{\partial}{\partial y}\frac{\partial v_y}{\partial x}\right)\right\}\\ &=\frac{\partial P}{\partial x}-\left\{\mu\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_x}{\partial y^2}\right)+\mu\frac{\partial}{\partial x}\left(\frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}\right)\right\}=\frac{\partial P}{\partial x}-\mu\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_x}{\partial y^2}\right)\end{aligned}$$

Addition of the parts yields the desired result. The derivation proceeds analogously for the second component of momentum.

In general, we can say that the divergence of the velocity vector is zero for incompressible fluids. The momentum equations, on the other hand, contain terms referring to convection, to stress power due to the spatial change of pressure, and to viscous friction.

The energy equation. The energy equation (with the enthalpy substituting for the internal energy) turns out to be

$$\begin{aligned}\rho v_x\frac{\partial h}{\partial x}+\rho v_y\frac{\partial h}{\partial y}&=v_x\frac{\partial P}{\partial x}+v_y\frac{\partial P}{\partial y}\\ &+2\mu\left[\left(\frac{\partial v_x}{\partial x}\right)^2+\left(\frac{\partial v_y}{\partial y}\right)^2\right]+\mu\left(\frac{\partial v_x}{\partial y}+\frac{\partial v_y}{\partial x}\right)^2-\frac{\partial j_{E,th,x}}{\partial x}-\frac{\partial j_{E,th,y}}{\partial y}\end{aligned}\tag{14.9}$$

This can be derived as follows. The derivation of the law of balance of energy can be obtained as follows. In two dimensions, the energy equation Equ.$(14.4)_3$ looks like this:

$$\begin{aligned}\rho v_x\frac{\partial u}{\partial x}+\rho v_y\frac{\partial u}{\partial y}+j_{pxx}{}^{(c)}\frac{\partial v_x}{\partial x}+j_{pxy}{}^{(c)}\frac{1}{2}\left(\frac{\partial v_x}{\partial y}+\frac{\partial v_y}{\partial x}\right)&\\ +j_{pyx}{}^{(c)}\frac{1}{2}\left(\frac{\partial v_y}{\partial x}+\frac{\partial v_x}{\partial y}\right)+j_{pyy}{}^{(c)}\frac{\partial v_y}{\partial y}+\frac{\partial j_{E,th,x}}{\partial x}+\frac{\partial j_{E,th,y}}{\partial y}&=0\end{aligned}$$

The four components of the momentum current density tensor (the conductive part) are the following

$$\begin{aligned}j_{pxx}{}^{(c)}&=P-2\mu\frac{\partial v_x}{\partial x}\\ j_{pxy}{}^{(c)}&=-\mu\left(\frac{\partial v_x}{\partial y}+\frac{\partial v_y}{\partial x}\right)\\ j_{pyx}{}^{(c)}&=-\mu\left(\frac{\partial v_y}{\partial x}+\frac{\partial v_x}{\partial y}\right)\\ j_{pyy}{}^{(c)}&=P-2\mu\frac{\partial v_y}{\partial y}\end{aligned}$$

Inserting these into the energy equation yields

$$\rho v_x \frac{\partial u}{\partial x} + \rho v_y \frac{\partial u}{\partial y} + \left(P - 2\mu \frac{\partial v_x}{\partial x} \right) \frac{\partial v_x}{\partial x} - \mu \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) \frac{1}{2} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right)$$
$$- \mu \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} \right) \frac{1}{2} \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} \right) + \left(P - 2\mu \frac{\partial v_y}{\partial y} \right) \frac{\partial v_y}{\partial y}$$
$$+ \frac{\partial j_{E,th,x}}{\partial x} + \frac{\partial j_{E,th,y}}{\partial y} = 0$$

The terms containing the pressure add up to zero because of the equation of balance of mass. The rest yields the result given in Equ.(14.9); as a last step, you must only introduce the specific enthalpy $h = u + P/\rho$.

14.1.4 The boundary layer approximations

Several approximations apply to the case of boundary layer flow. The consequences of steady-state incompressible flow have already been worked out. First, the law of balance of mass applies as derived above in Equ.$(14.8)_1$, namely:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \qquad \textbf{(14.10)}$$

Now, we take into account (1) that the speed of flow parallel to the flat surface (as in Fig. 14.1) should be considerably larger than that normal to it, and (2) that the gradients of velocity and of temperature in the *y*-direction are much larger than those in the *x*-direction. Moreover, we assume (3) the variation of pressure in the direction of flow to be small and (4) fluid properties to be constant. Then, as the first consequence of assumption (1), all terms in the second momentum equation Equ.$(14.8)_3$ involving the velocity in the normal direction are very small, leaving us with

$$\frac{\partial P}{\partial y} = 0$$

which means that the pressure should be approximately constant in the *y*-direction. In the first momentum equation, however, only the pressure gradient and the friction term involving the *x*-gradient of the parallel flow speed are small compared to the other terms—assumptions (1–3). This leads to

$$\rho v_x \frac{\partial v_x}{\partial x} + \rho v_y \frac{\partial v_x}{\partial y} = \mu \frac{\partial^2 v_x}{\partial y^2}$$

or

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2} \quad , \quad \nu = \mu/\rho \qquad \textbf{(14.11)}$$

where the ratio of the dynamic viscosity and the density of the fluid is called the *kinematic viscosity*. The energy equation, finally, attains a structure quite similar to the law of balance of momentum in the *x*-direction. In addition to the previous assumptions, we also assume (5) the effect of viscous production of entropy to be small, and (6) conductive heat transfer to essentially take place in the direction normal to the flow. This yields

$$\rho v_x \frac{\partial h}{\partial x} + \rho v_y \frac{\partial h}{\partial y} = k_E \frac{\partial^2 T}{\partial y^2} \quad \Rightarrow$$

$$\rho v_x \frac{\partial h}{\partial T}\frac{\partial T}{\partial x} + \rho v_y \frac{\partial h}{\partial T}\frac{\partial T}{\partial y} = k_E \frac{\partial^2 T}{\partial y^2}$$

If we take the enthalpy of the incompressible fluid to be a linear function of temperature; i.e., if

$$h = h_o + c_P\left(T - T_o\right)$$

we obtain the following relation:

$$v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2} \quad , \quad \alpha = \frac{k_E}{\rho c_P} \tag{14.12}$$

The quantity α is called the *thermal diffusivity* (which is proportional to the entropy diffusivity). If we compare this last result with Equ.(14.11), we can see that the kinematic viscosity plays the role of momentum diffusivity. Even though we use the energy equation for derivation, heat transfer is the transfer of entropy. On the basis of the fundamental quantities entropy and momentum, the thermal and mechanical phenomena in a boundary layer are structurally analogous. It is interesting to note that the diffusion of a chemical species at an interface can be treated in the same manner, leading to another deep analogy.[2] Obviously, diffusive transport occurs with entropy, momentum, and charge, as much as it does with chemical substances.

14.1.5 Nondimensional Form of the Boundary Layer Equations and Similarity Parameters

Solving the differential equations for boundary layer flow, even in their reduced form of Equations (14.10) – (14.12), is no small feat. Doing this for different geometries and fluids having different properties under varying conditions would be even more daunting. Therefore, it is imperative to be able to reduce the amount of work by introducing dimensionless forms of the equations and dimensionless groups of quantities and fluid properties. It is found that the results depend for a given geometry upon these dimensionless groups only.

First, we introduce the following dimensionless independent and dependent variables:

$$\begin{aligned} &x^* = x/L \quad , \quad y^* = y/L \\ &v_x^* = v_x/v_\infty \quad , \quad v_y^* = v_y/v_\infty \\ &T^* = \frac{T - T_s}{T_\infty - T_s} \end{aligned} \tag{14.13}$$

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[2] See, for example, Incropera and DeWitt, 1981.

Here, L is some characteristic length associated with the geometry of the body over which the fluid is flowing. In the case of a flat plate, we may take L to represent its length. With these quantities, the simplified boundary layer equations become

$$\begin{aligned}
&\frac{\partial v_x *}{\partial x *} + \frac{\partial v_y *}{\partial y *} = 0 \\
&v_x * \frac{\partial v_x *}{\partial x *} + v_y * \frac{\partial v_x *}{\partial y *} = \frac{1}{Re_L} \frac{\partial^2 v_x *}{\partial y *^2} \\
&v_x * \frac{\partial T *}{\partial x *} + v_y * \frac{\partial T *}{\partial y *} = \frac{1}{Re_L Pr} \frac{\partial^2 T *}{\partial y *^2}
\end{aligned} \tag{14.14}$$

where the dimensionless Reynolds and Prandtl numbers have been introduced:

$$\begin{aligned}
&\text{Reynolds number:} \quad Re_L = \frac{v_\infty L}{\nu} \\
&\text{Prandtl number:} \quad Pr = \frac{\nu}{\alpha}
\end{aligned} \tag{14.15}$$

The Reynolds number represents approximately the ratio of inertial to viscous effects in the fluid, while the Prandtl number is the ratio of the momentum and the thermal diffusivities. The Reynolds number can also be used to express the friction coefficient:

$$C_f = \frac{2}{Re_L} \left. \frac{\partial v_x *}{\partial y *} \right|_{y* = 0} \tag{14.16}$$

If the dimensionless variables are introduced in the relation for the heat transfer coefficient in Equ.(14.1), we obtain

$$h = \frac{k_{Ef}}{L} \left. \frac{\partial T *}{\partial y *} \right|_{y* = 0} \tag{14.17}$$

A third dimensionless group is introduced, which relates the convective heat transfer coefficient to the conductive one:

$$\text{Nusselt number:} \quad Nu = \frac{hL}{k_{Ef}} \tag{14.18}$$

As you can tell from the definition, this factor is the dimensionless temperature gradient at the surface of the solid body.

Results of the determination of convective heat transfer coefficients are now cast in the form of relations between the dimensionless groups which hold for a given geometry, independent of fluid properties and flow conditions as long as the basic restrictions apply (i.e., those restrictions which led to the reduced form of the differential equations). The dimensionless equations suggest that the x-velocity is some universal function of the dimensionless coordinates and the Reynolds number, the friction factor depends only upon $x*$ and the Reynolds number; and the dimensionless temperature may be obtained from a universal function of the coordinates, the Reynolds number and the Prandtl number. Therefore, for prescribed geometry, the Nusselt number is a universal function of the position along the surface, the Reynolds number, and the

Prandtl number:

$$Nu = f\left(x^*, Re_L, Pr\right) \tag{14.19}$$

For example, the equations can be integrated for laminar flow over a flat plate:

$$C_{f,x} = 0.664 Re_x^{-1/2} \quad , \quad Nu_x = 0.332 Re_x^{1/2} Pr^{1/3} \tag{14.20}$$

This holds as long as the Prandtl number is larger than 0.6.[3] The subscript *x* refers to the position in *x*-direction along the flat plate. The local Nusselt number Nu_x has to be integrated if we wish to obtain the average value up to position *x*. For this case, it turns out that the average value up to position *x* is twice the local value at *x*.

Naturally, other geometries and flow conditions lead to different and often much more complicated problems. Turbulent flow, for example, cannot be treated analytically, at least not without the introduction of additional strong assumptions. Turbulent mixing in the boundary layer leads to greatly increased thermal and momentum diffusivities[4] for which we do not have simple expressions, since they depend upon the state of motion and not just upon fluid properties. In many heat transfer applications of practical interest, experimental determination of the heat transfer coefficient is required. Fortunately, the dimensionless groups help to reduce the complexity of the problem just as they did in the theoretical example. In other words, as in the case of an analytical calculation, we should try to measure the Nusselt number in terms of the Reynolds and the Prandtl numbers to obtain empirical relations analogous to what we have seen in Equ.(14.20).

QUESTIONS

1. How is the entropy transfer coefficient at an interface defined?
2. The equations of balance, Equations (14.4), contain time derivatives. Why are they absent from Equations (14.8) and Equ.(14.9)?
3. In the derivation of Equ.(14.9), four components of the momentum current density tensor are listed. Why are there four components? How can the forms be motivated?
4. What is the importance of the non-dimensional groups introduced to describe boundary layer flows?

14.2 A STUDY OF SOLAR COLLECTORS

Basically, any object which absorbs the light of the Sun is a solar collector. Therefore, we should include in this list the leaves of trees, buildings, soil, the oceans, or photovoltaic cells, just to name a few. You can see the range of phenomena induced by the Sun's rays. The "collectors" may produce substances, they may lead to the flow of electric charge, or they may produce heat (i.e., entropy). Here we shall look only at the latter effect in simple technical devices.

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[3] See, for example, Incropera and DeWitt (1981), p. 313–318.

[4] Incropera and DeWitt (1981), p. 293–296.

A thermal solar collector is a device which absorbs a part of the solar radiation falling upon it, leading to entropy production in the absorber. If we let a fluid flow across the absorber, we may harness some of the entropy which has been created (Fig. 14.2). In the simplest possible geometrical arrangement, we have a flat absorber plate possibly made out of some thin metal sheet. We may then let a fluid (liquid or air) flow through a rectangular duct behind the absorber, with the fluid wetting its entire surface area. Commonly, the collector is insulated at the bottom, and a transparent cover is placed above the absorber plate; both devices reduce the loss of entropy to the environment. The ducts for fluid flow in the collector are often different from (and more complicated than) what we have assumed here, leading to more difficult geometrical arrangements for the transfer of heat between an absorber and fluid. This point will be further discussed below.

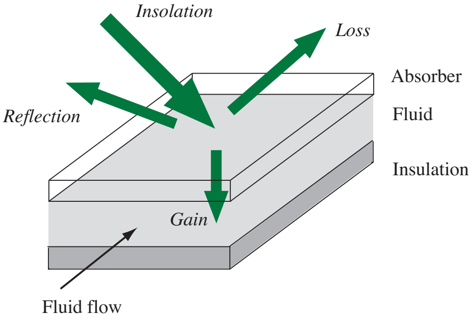

Figure 14.2: Simple flat-plate solar collector consists of a flat absorber plate (possibly including a cover for reducing the losses to the top). Absorption of solar radiation leads to the production of entropy in the plate. A fluid flowing across the bottom of the plate can carry away some of the entropy. The figure shows the simplest possible geometry for absorber and fluid flow. The fat arrows denote the energy fluxes with respect to the absorber.

Basically, a thermal solar collector of the type discussed here is a flow heater (see Chapter 8 for a treatment of uniform models of flow heaters). Unlike the models introduced in Chapter 8, the ones created here will take into account the spatial variation of temperature of the fluid in the duct.

14.2.1 The Balance of Energy for a Solar Collector

Fig. 14.2 shows the fluxes of energy with respect to the absorber. They will be used to express the balance of energy (and of entropy) with respect to the absorber. In a second step, we will perform the balance of energy with respect to the entire collector. First, we have the flux associated with solar radiation falling upon the collector.[5] As you know, unless the surface is a black body, only part of the radiation will be absorbed, while the rest will be reflected back to the environment. The ratio of radiation absorbed to radiation falling upon the surface defines the optical properties of a collector which depend upon the absorber, the cover, and the type of radiation. Usually, for the purpose of an overall balance, their combined effect is described by a factor known as the *transmission-absorption product* ($\tau\alpha$); see Section 9.4.1 and Chapter 16.

The losses of the collector plate to the environment, on the other hand, are calculated

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[5] Naturally, radiation falling upon the collector includes the radiation of the atmosphere as a body at or near environmental temperature. This contribution is not included with the solar irradiance $\mathcal{G}$, but rather with the losses of the collector to the environment.

in terms of a heat loss coefficient U_t (top loss coefficient). In the following analysis, we shall assume losses to occur only through the top of the collector. The last energy flux is due to convective transfer at the absorber-fluid interface. To describe its effect, we introduce the heat transfer coefficient from the plate to the fluid (abbreviated by U_{pf}). All three coefficients characterizing a collector, i.e., $(\tau\alpha)$, U_t, and U_{pf}, may depend upon the conditions under which it is operated.

If we collect all the terms, a steady-state balance of energy for the absorber takes the form (Fig. 14.3):

$$(\tau\alpha)\mathcal{G} - U_t\left(T_p - T_a\right) = U_{pf}\left(T_p - T_f\right) \tag{14.21}$$

The indices p and f refer to the absorber plate and the fluid, respectively. As usual, a stands for *ambient*. $\mathcal{G}$ is the total irradiance with respect to the surface of the collector. This equation holds for every point of the surface, with the temperatures of the fluid and the plate changing in the direction of fluid flow (but, for our simple geometry, not in the direction perpendicular to the flow). Naturally, we have a problem concerning the meaning of the temperatures T_f and T_p if we want to apply Equ.(14.21) directly for the entire collector of surface area A. In this case, just think of the temperatures as some appropriate average value for the respective system.

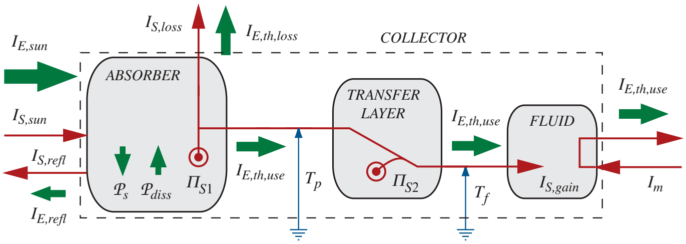


Figure 14.3: Process diagram for the collector showing fluxes of entropy and energy. Almost all the entropy transferred to the fluid and to the environment is produced in the system.

The equation of balance of entropy will be written below for the collector as the system. First, however, let us express the overall balance of energy. In this case, we have to include the convective currents of energy due to fluid flow into and out of the collector, while the flux from the plate to the fluid drops out:

$$c_p I_m\left(T_{f,out} - T_{f,in}\right) = A\left[(\tau\alpha)\mathcal{G} - U_t\left(T_{pm} - T_a\right)\right] \tag{14.22}$$

As just mentioned, in this equation T_{pm} represents the proper average value. Normally, we take both the temperature coefficient of enthalpy of the fluid and the pressure as constants, which permits us to use Equ.(8.60) for the convective current.

Since the temperature of the collector plate is not easily accessible, one replaces the temperature of the absorber in Equ.(14.22) using Equ.(14.21). As a result, the (average) temperature of the fluid appears in the law of balance:

$$I_{E,use} = A\frac{U_{pf}}{U_{pf} + U_t}\left[(\tau\alpha)\mathcal{G} - U_t\left(T_{fm} - T_a\right)\right]$$

$I_{E,use}$ is the useful energy current, i.e., the convective current with respect to the collector. The factor multiplying the term in parenthesis is called the *collector efficiency factor* and it is commonly abbreviated F'. Using this definition leads to the expression for the useful energy current in terms of the fluid temperature:

$$\begin{aligned} I_{E,use} &= AF'\Big[(\tau\alpha)\mathcal{G} - U_t\big(T_{fm} - T_a\big)\Big] \\ F' &= \frac{U_{pf}}{U_{pf} + U_t} \end{aligned} \tag{14.23}$$

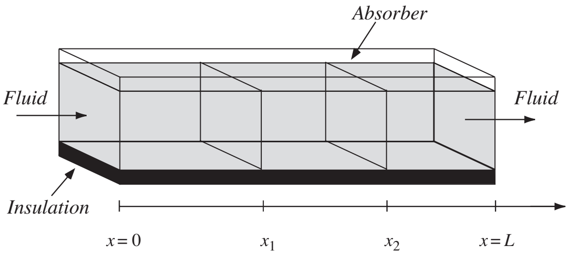
If you rewrite the efficiency factor in a slightly different form, you can see that it corresponds to the ratio of the thermal resistances between the absorber and the environment on the one hand, and between the fluid and the environment on the other.

Different fluid duct geometries. Usually, the geometrical arrangement of the fluid ducts is different from the simple case assumed so far. This holds especially for collectors using liquids for heat transfer. Therefore, if U_{pf} is still used for the heat transfer coefficient from metal to fluid, the collector efficiency factor F' cannot be computed as done in Equ.(14.23). Take the case of a liquid flowing through thin pipes attached to the absorber. Obviously, heat has to flow through the absorber sheet to the pipes before it can enter the fluid. The efficiency will be reduced both because of this process and because of the fact that the fluid surface may be smaller than that of the flat absorber. The efficiency factor will depend not only upon the heat transfer coefficient, but also upon the distance between the pipes, the thickness and the conductivity of the absorber sheet, and the inner surface area of the pipes carrying the fluid. Therefore, the task of computing the efficiency factor can be quite complicated.[6] However, with a known efficiency factor, a reduced heat transfer coefficient can be calculated and used as in the equations presented above (Example 14.2).

14.2.2 Temperature Distribution in the Direction of Fluid Flow

Equ.(14.23) holds only with the appropriate average of the temperature of the fluid as an overall balance of energy. We may approximate this value by the arithmetic average of the fluid temperatures at the inlet and the outlet of the collector (as shown in Example 14.1). A better expression, however, requires considering the change of temperatures in the direction of fluid flow in the collector. This is achieved by treating the example as a continuous problem in one spatial dimension (Fig. 14.4).

Figure 14.4: Fluid flowing through the collector heats up in the direction of flow. The law of balance of energy for the control volume between x_1 and x_2 leads to an expression for the temperature as a function of position.



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[6] See for example Duffie and Beckman (1991), Chapter 6.

The law of balance of energy for the control volume of length x_2–x_1 can be used to derive the expression for the temperature of the fluid as a function of position x. The fluid portion in the control volume is heated from above, and it flows into and out of the volume. If we use Equ.(14.23) in the form

$$j_{E,use} = F'\left[(\tau\alpha)\mathcal{G} - U_t\left(T_f(x) - T_a\right)\right]$$

the law of balance for the control volume is

$$c_P I_m\left(T_f(x_2) - T_f(x_1)\right) = F'\int_{x_1}^{x_2} W\left[(\tau\alpha)\mathcal{G} - U_t\left(T_f(x) - T_a\right)\right]dx$$

Here, W is the width of the collector. The left-hand side represents the convective current due to the fluid entering and leaving, while the right-hand side is the integral of the energy current density over the top surface area of the control volume. The equation transforms into the differential equation

$$c_P I_m \frac{dT_f}{dx} = F'W\left[(\tau\alpha)\mathcal{G} - U_t\left(T_f(x) - T_a\right)\right] \tag{14.24}$$

whose solution is

$$T_f(x) = \frac{(\tau\alpha)\mathcal{G}}{U_t} + T_a - \left[\frac{(\tau\alpha)\mathcal{G}}{U_t} + T_a - T_{f,in}\right]\exp\left(-\frac{F'U_t W}{c_P I_m}x\right) \tag{14.25}$$

If we take the value of T_f at the outlet, subtract it at the inlet, and multiply by the product of c_P and I_m, we obtain the useful energy current:

$$I_{E,use} = A\frac{c_P I_m}{AU_t}\left[1 - \exp\left(-\frac{F'U_t A}{c_P I_m}\right)\right]\left[(\tau\alpha)\mathcal{G} - U_t\left(T_{f,in} - T_a\right)\right]$$

Basically, this result represents a transformation of the expression used previously in Equ.(14.23) where the mean fluid temperature is replaced by the temperature of the fluid at the inlet to the collector. As a consequence, the collector efficiency factor F' is replaced by the *heat removal factor* F_R:

$$I_{E,use} = AF_R\left[(\tau\alpha)\mathcal{G} - U_t\left(T_{f,in} - T_a\right)\right] \tag{14.26}$$

where

$$F_R = \frac{c_P I_m}{AU_t}\left[1 - \exp\left(-\frac{F'U_t A}{c_P I_m}\right)\right] \tag{14.27}$$

Equ.(14.26) allows us to calculate the useful energy current of a flat-plate solar collector in terms of environmental parameters, the current of mass through the collector, and the inlet temperature of the fluid. The collector can be characterized by two parameters, $F_R(\tau\alpha)$ and $F_R U_t$; considering that F_R includes the efficiency factor, we may say that there are three values defining the device—$(\tau\alpha)$, U_t, and F'. In practical cases, these parameters are measured (Example 14.1).

14.2.3 The Balance of Entropy for a Solar Collector

While it is convenient to obtain the results concerning the thermal performance of a collector in terms of the balance of energy, this law alone does not suffice for a complete description of its operation. If we wish to include the evaluation of irreversibilities in our analysis, we have to perform a balance of entropy for the collector.

An overall balance is written quite easily. Again, we shall treat steady-state operation. Essentially, we take four currents of entropy with respect to the collector as a whole into consideration, as well as the rate of production of entropy. The four currents are due to radiation, heat loss, and the fluid entering and leaving the collector. Production is the result of the absorption of radiation, heat transfer to the fluid and heat flow into the environment. The overall balance then takes the form

$$\Pi_S = I_{S,rad} + I_{S,loss} + I_{S,fluid,in} + I_{S,fluid,out} \tag{14.28}$$

If we properly place the boundary of the control volume, all sources of irreversibility will be included. In particular, this means that for the incoming radiation we take the surface of the cover of the collector, while for the losses the boundary will coincide with the environment at ambient temperature. Now the terms in Equ.(14.28) take the following form:

$$\Pi_S = -A(\tau\alpha)\mathcal{G}\frac{4}{3T_s} + \frac{1}{T_a}\left|I_{E,loss}\right| + \left(s_{f,out} - s_{f,in}\right)\left|I_m\right| \tag{14.29}$$

This result allows us to calculate the rate of production of entropy since, in principle, all the other quantities are known. As before, T_s is the temperature of solar radiation. The energy current due to the loss to the environment can be computed using the balance of energy expressed in Equ.(14.26), while the specific entropy of the fluid at the inlet and the outlet is obtained in terms of the values of temperature and pressure at the respective points. The net convective current of entropy can be calculated for constant pressure and constant value of the temperature coefficient of enthalpy according to Equ.(8.9) with Equ.(8.11) or Equ.$(8.52)_3$.

14.2.4 Dynamical Model of a Solar Collector

A solar collector is a dynamical system, storing entropy and energy. A steady-state analysis might therefore not be appropriate. However, coupled with a heat storage element of much higher capacity, the simplification can be justified, although, in some cases, it might be necessary to consider the dynamical behavior of the collector.

We may start with the law of balance of energy. In analogy to what we have seen in previous chapters, we can write

$$\begin{aligned} C_c\frac{dT_f}{dt} &= F'\left[(\tau\alpha)\mathcal{G} - U_t\left(T_f - T_a\right)\right] - c_P I_m\left(T_{f,out} - T_{f,in}\right) \\ T_f &= \left(T_{f,in} + T_{f,out}\right)/2 \end{aligned} \tag{14.30}$$

Here, C_c is the temperature coefficient of energy of the collector, or possibly of a collector element. (In the latter case, the collector can be thought of as composed of several elements put in series which improves upon the approximation.) This value must include the absorber, the cover, the fluid, and the insulation. Equ.(14.30) represents a particularly simple approximation of the terms in the equation of balance of energy of a uniform collector or collector element. The temperature of the element is approximated by the mean temperature of the fluid in it. Typical values used for C_c are between 5000 J/K and 10000 J/K for one square meter of collector area for a collector with liquid as heat transfer fluid.

QUESTIONS

5. What is the meaning of the power of solar radiation ($\mathcal{P}_s$) included in the diagram on the left of Fig. 14.3? Why is it not possible to calculate this quantity in analogy to typical expression for the power of a process (as introduced in Chapter 2)?
6. Under what circumstances is the energy current from the (hot) absorber to the fluid in the collector equal to the net convective energy current of the fluid flowing through the collector?
7. Are all sources of irreversibility included in the expression for the entropy production rate in a collector given in Equ.(14.29)?
8. Consider a thermal solar collector hooked up to a storage tank for the heated fluid. Why is it possible (and often sensible) to treat the collector as being in (pseudo) steady-state having a balance of energy given by Equ.(14.26).
9. Why does Equ.(14.26) lead to a simpler—and actually more accurate—expression for dynamical models of collectors and (hot) fluid storage tanks than Equ.(14.23)?

EXAMPLE 14.1. Measuring the characteristic parameters of a flat-plate collector.

Measurements of the thermal efficiency of a flat-plate solar collector are made for conditions where the collector directly faces the Sun. The efficiency is plotted as a function of

$$x = \frac{T_{f,am} - T_a}{\mathcal{G}}$$

where $T_{f,am}$ is the arithmetic mean of the fluid inlet and outlet temperatures. Measurements were performed with a constant flux of mass of 40 liters per hour per square meter of collector area (see Figure Ex.1). The temperature coefficient of enthalpy of the fluid is 3800 J/(K·kg).

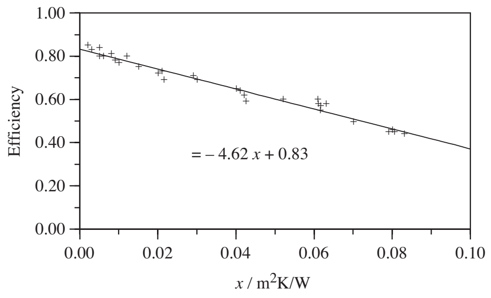

Figure Ex.1

(a) Derive the expression for the efficiency of a solar collector as a function of x. (b) Determine the values of $F_R U_t$ and $F_R(\tau\alpha)_n$ for the values shown in the accompanying graph. The index n

with the transmission-absorption product stands for normal incidence of solar radiation. (c) It is known from detailed calculations that the collector efficiency factor F' is 0.92. Calculate the actual optical efficiency $(\tau\alpha)_n$ and the actual heat loss factor U_t.

*SOLUTION: (*a) The thermal efficiency of the collector is defined as the ratio of the energy delivered by the heated fluid and the energy incident upon the collector:

$$\eta = I_{E,use} / (A\,\mathcal{G})$$

The useful energy current should be expressed similarly to Equ.(14.23), with F' replaced by F_{am} since T_{fm} has been replaced by $T_{f,am}$:

$$I_{E,use} = AF_{am}\left[(\tau\alpha)_n\,\mathcal{G} - U_t\left(T_{f,am} - T_a\right)\right]$$

We may expect the efficiency factor F_{am} to be nearly equal to F', considering that the arithmetic mean of the collector fluid temperature will not deviate all that much from the proper average value. Therefore, the efficiency turns out to be

$$\eta = F_{am}(\tau\alpha)_n - F_{am}U_t\,\frac{T_{f,am} - T_a}{\mathcal{G}}$$

which is close to

$$\eta = F'(\tau\alpha)_n - F'U_t\,\frac{T_{f,am} - T_a}{G}$$

This shows that efficiency data plotted as a function of the coefficient x introduced above should yield a linear relation if the collector parameters are independent of the conditions under which the device is operated.

(b) The data plotted in the graph yield approximate values of $F'(\tau\alpha)_n$ and $F'U_t$. Approximating the measured values by a least-squares linear fit, we obtain

$$F'(\tau\alpha)_n = 0.83$$
$$F'U_t = 4.62\,\mathrm{W}/\left(\mathrm{K}\cdot\mathrm{m}^2\right)$$

Since the measured values of the efficiency were obtained with the collector directly facing the Sun, we get the transmission-absorption product for normal incidence. We transform the expressions to calculate the desired parameters of the collector. A simple way of doing this is the following. Since the heat removal factor F_R is used with the inlet temperature of the fluid in Equ.(14.26) for the useful energy current, we should replace the arithmetic mean of the fluid temperature by the inlet value, which leads to

$$I_{E,use} = AF'\left[1 + \frac{1}{2}\frac{F'U_tA}{c_pI_m}\right]^{-1}\left[(\tau\alpha)_n\,\mathcal{G} - U_t\left(T_{f,in} - T_a\right)\right]$$

You can show that this is an approximation to the expression given in Equ.(14.26) with the exact heat removal factor of Equ.(14.27). A comparison of this result with the first equation for the useful energy current yields

$$F_R(\tau\alpha)_n = F'(\tau\alpha)_n\left[1 + \frac{1}{2}\frac{F'U_tA}{c_pI_m}\right]^{-1}$$

and

$$F_R U_t = F'U_t \left[1 + \frac{1}{2} \frac{F'U_t A}{c_p I_m} \right]^{-1}$$

The numerical results turn out to be

$$F_R(\tau\alpha)_n = 0.83 \cdot \left[1 + \frac{4.62}{2 \cdot 3800 \cdot 40/(3600)} \right]^{-1} = 0.79$$

$$F_R U_t = 4.62 \cdot \left[1 + \frac{4.62}{2 \cdot 3800 \cdot 40/(3600)} \right]^{-1} \mathrm{W}/\left(\mathrm{K} \cdot \mathrm{m}^2\right) = 4.38\,\mathrm{W}/\left(\mathrm{K} \cdot \mathrm{m}^2\right)$$

(c) Knowing the collector efficiency factor, the actual collector parameters can be calculated:

$$F'(\tau\alpha)_n = 0.83 \qquad \Rightarrow \quad (\tau\alpha)_n = 0.90$$

$$F'U_t = 4.62\,\mathrm{W}/\left(\mathrm{K} \cdot \mathrm{m}^2\right) \qquad \Rightarrow \quad U_t = 5.02\,\mathrm{W}/\left(\mathrm{K} \cdot \mathrm{m}^2\right)$$

This is a collector with a fairly high optical efficiency, but with a mediocre heat loss factor.

EXAMPLE 14.2. A thermosyphon collector.

In a thermosyphon collector, the fluid circulates without a pump. Instead of forced convection, the process operates because of density gradients in the differentially heated fluid. (See Fig. Ex.2 below.)

Assume the fluid in the tank to be well mixed, and approximate the temperature of the fluid in the rising part of the hydraulic circuit, including the collector, by the average temperature. Also assume the density of the fluid to be a linear function of temperature. Fluid resistance may be modeled by the law of Hagen and Poiseuille. Calculate the steady state flux of mass through the collector.

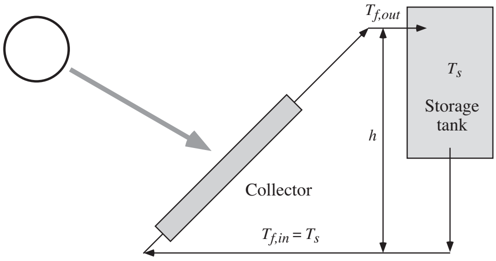

Figure Ex.2

SOLUTION: The natural circulation is the result of different hydrostatic pressures in the rising and falling parts of the hydraulic circuit. In the steady state, the driving pressure difference is equal in magnitude to the one resulting from flow resistance:

$$\Delta P = \Delta\rho g h$$

$$I_V = \frac{1}{R_V} \Delta P$$

$\Delta\rho$ is the difference of densities of the fluid in the two parts of the circuit. It can be expressed as follows:

$$\Delta\rho = b\,\Delta T = b\left[\frac{1}{2}\left(T_{f,out} + T_{f,in}\right) - T_s\right]$$

where $T_{f,in}$ is the temperature T_s of the fluid in the storage tank. The parameter b is the temperature coefficient of the density of the fluid. The collector outlet temperature is calculated using the balance of energy expressed by Equ.(14.23):

$$c_p I_m\left(T_{f,out} - T_{f,in}\right) = AF'\left[(\tau\alpha)\mathcal{G} - U_t\left(\frac{1}{2}\left(T_{f,out} + T_{f,in}\right) - T_a\right)\right] + \Delta P I_V$$

The last term is the rate of energy input to the system as a consequence of the natural circulation; the energy comes from the gravitational field. It turns out that this term is very small compared to the others in the equation of balance of energy; it will therefore be neglected.

Now, the temperatures can be eliminated from the last equation using the first three relations. This leaves us with a quadratic equation for the volume flux:

$$\frac{2c_p\rho R_v}{bgh} I_V^2 + \frac{AF'U_t R_v}{bgh} I_V - AF'\left[(\tau\alpha)\mathcal{G} - U_t\left(T_s - T_a\right)\right] = 0$$

This demonstrates that the circulation depends upon the instantaneous temperature of the fluid in the storage tank. As the fluid temperature in the tank rises during charging, the circulation is found to decrease. Since, compared to the storage unit, the collector and hydraulic circuit probably react quickly to changing conditions, the steady-state analysis appears to be appropriate.

EXAMPLE 14.3. Charging and discharging of seasonal ground heat storage.

A spatially uniform model of a cylindrical underground heat storage element hooked up to a solar collector field for charging during summer, and with a building for discharging during winter, can be used to approximate the much more complicated spatially continuous problem (see Figure Ex.3).

The system consists of a collector field of surface area A_c and described by the usual collector parameters. Pipes carry the heated fluid to the ground storage unit which is a cylinder of radius R and length L. (See the figure below.) There are N parallel pipes, each heating an interior cylinder. (The interior cylinders uniformly cover the storage unit.) The ground storage cylinder loses heat to the surroundings. Discharging in winter occurs through the floor heating system of a building.

The model is described as follows. Charging is done during the six months from spring to fall. The irradiance is twice the average value for half the time (roughly $8 \cdot 10^6$ seconds), i.e., the usual amount of energy is delivered to the collectors. Collector parameters are assumed to be constant, as is the flux of mass of the collector fluid. The fluid, which flows through N parallel pipes, is cooled from $T_{f,out}$ to $T_{f,in}$ while flowing down through the storage unit (*in* and *out* refer to the collector).

The storage in the ground is supposed to have uniform values of density, temperature coefficient of energy, and thermal conductivity, and a single value of temperature at any time. Heat flow should be radial only (no heat loss through the top or bottom of the cylinder). Delivery of heat to each interior cylinder is described by an average value UA_{int} which is calculated from the fluid in the pipe through half of the radius of the cylinder. Heat loss from the entire storage unit to the surroundings is calculated with a value UA_{store}, representing a thick cylindrical shell with radii which are half and twice the radius R of the storage unit. The temperature of the ground surrounding the storage unit is assumed to be constant.

During discharging in winter, parameters for the storage space are the same. Heat is delivered at a constant temperature to rooms in the building. The value of UA_{floor} of the floor heating system is given.

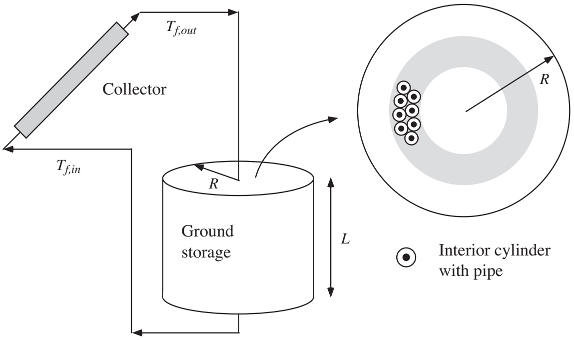

Figure Ex.3

(a) Derive the differential equation of the temperature of the storage unit as a function of time for charging. Present its analytical solution. (b) With an initial temperature of the ground storage unit at the beginning of winter, derive the temperature as a function of time. (c) Give an expression for the total amount of entropy produced for an entire cycle of charging and discharging which carries the storage from an initial temperature back to the same value. (d) If the only parameter varied in the entire system is the length L of the storage unit, do you expect a minimum of entropy production for a cycle for a particular value of L?

Neglect pipe losses and energy required for pumping the fluids during charging and discharging.

SOLUTION: (a) The storage unit receives energy from the collector fluid and loses energy to the ground. The overall balance of energy for charging therefore takes the form

$$C_s \frac{dT_s}{dt} = \left|I_{E,fs}\right| - \left|I_{E,loss}\right|$$

with

$$\begin{aligned}
C_s &= \pi R^2 L \rho c_s \\
\left|I_{E,fs}\right| &= UA_{fs}\left(T_{fm} - T_s\right) \\
\left|I_{E,loss}\right| &= UA_{store}\left(T_s - T_{ground}\right)
\end{aligned}$$

For T_{fm} we take the arithmetic mean of the fluid inlet and outlet temperatures

$$T_{fm} = \frac{1}{2}\left(T_{f,in} + T_{f,out}\right)$$

which also depend upon the performance of the collectors:

$$\begin{aligned}
\left|I_{E,fs}\right| &= A_c F_R\left[(\tau\alpha)\mathcal{G} - U_t\left(T_{f,in} - T_a\right)\right] \\
\left|I_{E,fs}\right| &= c_P I_m\left(T_{f,out} - T_{f,in}\right)
\end{aligned}$$

T_a is the average ambient temperature for the period of charging. The value of UA_{fs} for heat transfer from the fluid to an interior cylinder is given by

$$UA_{fs} = NUA_{int}$$
$$UA_{int} = 2\pi L\left[\frac{1}{r_{pipe}U_{pipe}} + \frac{1}{k}\ln\left(\frac{0.5R_{int}}{r_{pipe}}\right)\right]^{-1}$$

where R_{int} is the radius of an interior cylinder

$$R_{int} = \frac{1}{\sqrt{N}}R$$

and r_{pipe} and U_{pipe} are the radius and the heat transfer coefficient of the pipe; k is the thermal conductivity of the ground. The value of UA_{store} is calculated simply:

$$UA_{store} = 2\pi Lk\left[\ln\left(\frac{2R}{R/2}\right)\right]^{-1}$$

There are three equations for the energy current $I_{E,fs}$ and one for the arithmetic mean of the fluid temperature. First, we can eliminate $T_{f,out}$ and obtain an expression for $T_{f,in}$:

$$T_{f,in} = T_s + \left(\frac{1}{AU_{fs}} - \frac{1}{2c_P I_m}\right)\left|I_{E,fs}\right|$$

If we plug this into the expression for the energy current delivered by the collector, we arrive at

$$\left|I_{E,fs}\right| = B\left[(\tau\alpha)\mathcal{G} - U_t\left(T_s - T_a\right)\right]$$
$$B = \left(\frac{1}{A_c F_R} + \frac{U_t}{AU_{fs}} - \frac{U_t}{2c_P I_m}\right)^{-1}$$

This looks like a slightly different version of the equation for the energy delivered by a collector; note that the variable temperature occurring is the temperature T_s of the storage unit. Now, the differential equation for T_s is given by

$$\frac{dT_s}{dt} = a - bT_s$$

where

$$a = \frac{1}{C_s}\left(B\left[(\tau\alpha)\mathcal{G} + U_t T_a\right] + UA_{store}T_{ground}\right)$$
$$b = \frac{1}{C_s}\left(BU_t + UA_{store}\right)$$

The analytical solution of this simple differential equation is

$$T_s(t) = \frac{a}{b} - \left(\frac{a}{b} - T_{so}\right)\exp(-bt)$$

Here, T_{so} is the initial value of the temperature of the storage unit. Remember that the parameter t runs for only half the time span of charging, since we use twice the average insolation. (This models the fact that the Sun shines for only half the day.)

(b) The process of discharging is modeled similarly using the equation of balance of energy for the uniform storage space:

$$C_s \frac{dT_s}{dt} = -\left|I_{E,fs}\right| - \left|I_{E,loss}\right|$$

The energy currents are calculated as follows:

$$\left|I_{E,fs}\right| = UA_{fs}\left(T_s - T_{fm}\right)$$
$$\left|I_{E,loss}\right| = UA_{store}\left(T_s - T_{ground}\right)$$

This time, however, the energy current $I_{E,fs}$ also obeys the expression

$$\left|I_{E,fs}\right| = UA_{floor}\left(T_{fm} - T_{building}\right)$$

Combining all the information yields the following differential equation

$$\frac{dT_s}{dt} = f - gT_s$$

with

$$f = \frac{1}{C_s}\left(DUA_{fs}T_{building} + UA_{store}T_{ground}\right)$$
$$g = \frac{1}{C_s}\left(DUA_{fs} + UA_{store}\right)$$
$$D = \left(1 + \frac{UA_{fs}}{UA_{floor}}\right)^{-1}$$

which has the simple analytic solution

$$T_s(t) = \frac{f}{g} - \left(\frac{f}{g} - T_{ss}\right)\exp(-gt)$$

where T_{ss} is the initial temperature for discharging, which is the temperature of the storage unit at the end of summer.

(c) If you consider a system including the collectors, the storage unit, and the floor of the building, you will see that there are three currents of entropy and energy (each) leaving the system, while one is entering (associated with solar radiation). If we neglect the entropy delivered with the light of the Sun, the total amount of entropy produced in one cycle of the system can be written as follows:

$$S_{prod} = \frac{\left|E_{th,coll.loss}\right|}{T_a} + \frac{\left|E_{th,store.loss}\right|}{T_{ground}} + \frac{\left|E_{th,building}\right|}{T_{building}}$$

The integrated form of the balance of energy for the period of charging is given by

$$A_c(\tau\alpha)\mathcal{G}t_{charge} = \left|E_{th,coll.loss}\right| + \left|E_{th,store.loss}\right|_{charge} + C_s\left(T_{s,final} - T_{so}\right)$$
$$\left|E_{th,store.loss}\right|_{charge} = \int_{charge} UA_{store}\left(T_s - T_{ground}\right)dt$$

This allows for all relevant quantities to be computed for the process of charging. For discharging, we similarly obtain:

$$C_s\left(T_{s,\,final} - T_{so}\right) = \left|E_{th,\,store.loss}\right|_{discharge} + \left|E_{th,\,building}\right|$$

$$\left|E_{th,\,store.loss}\right|_{discharge} = \int_{discharge} UA_{store}\left(T_s - T_{ground}\right)dt$$

(d) Changing the length of the cylindrical storage unit (while leaving all other parameters untouched) will result in different storage temperatures. Increasing the length will decrease the maximum temperature reached. Now, having a high temperature after charging is going to increase losses (both from the collectors and from the storage to the ground). Very low storage temperatures, on the other hand, will make it difficult to discharge the unit. We should expect an optimal performance of the system for some value of *L*. Numerical calculations show that this is indeed the case. As we should expect, heating of the house will be optimal for minimal total entropy produced.

14.3 HEAT EXCHANGERS

Transferring heat from one system to another is a common task in engineering, and having to do so efficiently is becoming more and more important in applications such as energy engineering. Basically, any device which lets heat pass from one side to the other may be considered to be a heat exchanger. However, we normally speak of heat exchangers if heat is to be passed from a hot fluid stream to a colder one. In many cases, heat exchangers have to be used if different fluids are needed at different stages of operation in thermal equipment. There are many basic heat exchanger designs which differ in their geometrical arrangements, in the fluids used, and in the processes undergone by the fluids when they emit or absorb heat. Well known examples of heat exchangers are radiators for heating rooms or cooling of car engines, or the steam generators used in power plants where steam is to be produced using a fluid heated by the Sun or by a nuclear reactor.

14.3.1 The Principle of Operation of Heat Exchangers

As an example of a particularly simple geometrical arrangement, consider a counter-flow heat exchanger with the two fluids passing through ducts in opposite directions (Fig. 14.5) while heat flows from the hotter to the cooler body. Imagine both fluids to flow through thin but wide and long rectangular ducts separated by a wall which is re-

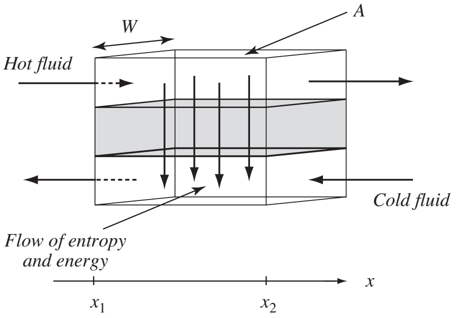

Figure 14.5: In the simplest possible geometrical arrangement, two fluids flowing through rectangular ducts exchange heat across the common flat surface. If the temperature of the fluids is allowed to vary only in the direction of flow, we have a one-dimensional problem. In a counter-flow heat exchanger, the fluids pass each other in opposite directions.

sponsible for the transfer of heat. Assume the temperature of each fluid to vary only in the x-direction.

The temperature distribution in the fluids as a function of position is sketched in Fig. 14.6. The temperature of the hotter fluid flowing in the upper duct decreases in the direction of x, while the hotness of the cooler fluid increases in the opposite direction. Naturally, the temperature of the upper fluid must always be higher than the corresponding value for the lower one.

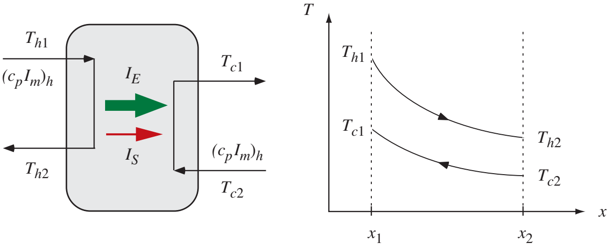

Figure 14.6: Flow diagram of counter-flow heat exchangers (left). The levels of the fluid currents symbolically represent the fact that heat is transferred from a higher to a lower thermal level. The temperature profiles of the two fluid streams have the forms shown (right). In counter-flow heat exchangers, the temperature difference between the fluids does not vary as strongly as in other arrangements.

In a parallel-flow heat exchanger, the fluids enter and leave the device on the same side. At the point where they enter, the fluids have the largest difference of temperatures (Fig. 14.7). This difference then decreases in the direction of flow, a situation which is different from that of a counter-flow heat exchanger.

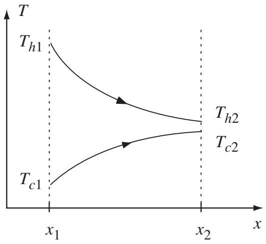

Figure 14.7: In a parallel-flow heat exchanger, the temperature difference between the fluids decreases in the direction of flow. The largest value of the difference occurs at the inlet to the exchanger. Usually, counter-flow heat exchangers are better than the parallel-flow type.

The main factors which determine the quality of a heat exchanger are the surface area through which the two fluids exchange entropy and energy, and the heat transfer coefficients for the exchange of heat between the fluids and the wall separating them. (Assuming that the wall does not add much to thermal resistance, the two convective heat transfer coefficients determine the outcome.) At each point of the surface the energy current density is given by the total local heat transfer coefficient and the local difference of the temperatures of the fluids. Since the temperature difference is variable over the surface, the total energy flux from one side of the exchanger to the other is commonly expressed in terms of an average product of surface area and transfer coefficient Ah, and a mean temperature difference ΔT_m:

$$I_E = Ah\Delta T_m \tag{14.31}$$

(Note that here and in the following equations, ΔT is taken as a positive quantity for positive flow.) The first of these factors depends upon the nature of heat transfer between the fluids and the wall separating them, and on the heat exchanger geometry, while the mean temperature difference[7] is a function of the inlet and outlet temperatures of the fluid and of the geometrical arrangement of the fluid currents. Naturally, the energy current being transferred is equal in magnitude to the difference of the convective energy fluxes associated with each of the fluids entering and leaving the heat exchanger. Therefore we can write:

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[7] For reasons which will become clear shortly, this temperature difference often is called the *log mean temperature difference*.

$$\begin{aligned} I_E &= \left(c_P I_m\right)_h \left(T_{h1} - T_{h2}\right) \\ I_E &= \left(c_P I_m\right)_c \left(T_{c1} - T_{c2}\right) \end{aligned} \tag{14.32}$$

The subscript *h* refers to the hotter of the two fluids, while *c* denotes the cooler one; the product of temperature coefficient of enthalpy and of the current of mass is generally called the "capacitance flow rate."

14.3.2 Heat Exchanger Effectiveness

The heat exchangers we are going to study will all be "ideal" in the sense that they are not supposed to lose any entropy to the surroundings; in other words, all the heat given up by the hotter fluid will be taken up by the second, cooler one. The exchange of entropy between the fluids, however, cannot be ideal since entropy is produced as a result of the transfer from higher to lower temperatures. The quality of a heat exchanger is therefore expressed in terms of a factor called the heat exchanger effectiveness. This is defined as the ratio of the actual transferred energy current and the current which could be passed between the fluids under ideal circumstances, i.e., if no temperature difference were needed:

$$\varepsilon = \frac{I_E}{\left(c_P I_m\right)_{min} \left(T_{h1} - T_{c2}\right)} \tag{14.33}$$

The latter of these quantities is determined by the largest temperature difference found and by the smaller of the two capacitance rates. It should be clear that the effectiveness of a heat exchanger depends upon the heat transfer factors and upon the capacitance rates of the fluids. At this point, we will simply state the result for counter-flow and parallel-flow exchangers (a derivation for the balanced counter-flow type will be given below). In the case of *counter-flow heat exchangers*, the effectiveness is given by

$$\varepsilon = \frac{1 - \exp\left(-NTU\left(1 - C^*\right)\right)}{1 - C^* \exp\left(-NTU\left(1 - C^*\right)\right)} \tag{14.34}$$

where

$$\begin{aligned} C^* &= \frac{\left(c_P I_m\right)_{min}}{\left(c_P I_m\right)_{max}} \\ NTU &= \frac{Ah}{\left(c_P I_m\right)_{min}} \end{aligned} \tag{14.35}$$

The coefficient *NTU* is called the number of transfer units. This result does not apply if the two capacitance rates are equal. Under these special circumstances, the effectiveness of the counter-flow heat exchanger must be calculated according to

$$\varepsilon = \frac{NTU}{1 + NTU} \tag{14.36}$$

If the capacitance flow rates are equal, the heat exchanger is said to be *balanced*. The equation for the effectiveness of *parallel-flow heat exchanger*s is the following:

$$\varepsilon = \frac{1 - \exp\left(-NTU\left(1 + C^*\right)\right)}{1 + C^*} \tag{14.37}$$

The definition of the factors in this result is the same as the one presented for counter-flow exchangers in Equ.(14.35).

14.3.3 The Balance of Energy

The derivation of the governing differential equations is another example of the approach we used for flat-plate solar collectors. First, we are going to develop the appropriate equations of balance in integral form for an entire system from which the differential equations will be derived.

Consider one of the ducts of the counter-flow heat exchanger or a piece thereof as depicted in Fig. 14.5. In such a system, we have three currents of entropy and the associated fluxes of energy, namely the convective currents entering and leaving a duct, and the conductive flow from the upper to lower duct through the wall separating the fluids. In the steady state, the balance of energy takes the following form:

$$c_P I_m \left(T_2 - T_1\right) + \int_{x_1}^{x_2} W \, j_E(x) dx = 0 \tag{14.38}$$

Remember that W is the width of the duct. This expression holds for both ducts if we apply the proper signs to the two cases.

The sum of the convective fluxes may be expressed in terms of the mass currents, the temperature coefficients of energy of the fluids, and the temperatures at the ends of the ducts. The conductive flux is the integral of the flux density over the surface of a duct. The flux density can be calculated using the transfer coefficient h and the temperature difference between the fluids of the upper and the lower ducts at position x:

$$j_E(x) = h(x)\left(T_h(x) - T_c(x)\right) \tag{14.39}$$

If we apply this relation to the fluids in the two ducts, we obtain

$$\begin{aligned} \left(c_P I_m\right)_h \left(T_{h2} - T_{h1}\right) + \int_{x_1}^{x_2} W \, h\left(T_h(x) - T_c(x)\right) dx = 0 \\ \left(c_P I_m\right)_c \left(T_{c1} - T_{c2}\right) - \int_{x_1}^{x_2} W \, h\left(T_h(x) - T_c(x)\right) dx = 0 \end{aligned} \tag{14.40}$$

Now we divide each of these equations by the difference of the positions of the end and the beginning of the ducts, i.e., by $x_2 - x_1$, and take the limit for very small Δx. In the first term of either equation we get the derivative of the temperature of the fluid with respect to position. We recover the integrand from the second term. The resulting differential equations then look like

$$\begin{aligned} \left(c_P I_m\right)_h \frac{dT_h}{dx} + W \, h\left(T_h(x) - T_c(x)\right) = 0 \\ \left(c_P I_m\right)_c \frac{dT_c}{dx} + W \, h\left(T_h(x) - T_c(x)\right) = 0 \end{aligned} \tag{14.41}$$

These are two coupled differential equations for T_h and T_c as unknown functions of position. The system of equations represents a two-point boundary value problem. Usually, the temperature of the fluids at their respective inlets would be given, and the variation of temperature with position is then calculated.

14.3.4 Derivation for Balanced Counter-Flow Heat Exchangers

The derivation of the following equations can be carried over to more general examples. We begin by subtracting Equ.(14.41)$_2$ from Equ.(14.41)$_1$ to obtain a differential equation for the difference between the fluid temperatures. For balanced heat exchangers, the two capacitance flow rates are equal; i.e.,

$$\left(c_P I_m\right)_h = \left(c_P I_m\right)_c$$

which leads to

$$\frac{d\left(T_h - T_c\right)}{dx} = 0 \tag{14.42}$$

This tells us that the temperature difference between the two fluids is the same at every point in the direction of flow. We now apply the expressions for the currents of energy according to Equations (14.31) and (14.32). Noting that the temperature of the hot fluid at the outlet is equal to the value of the temperature of the cold fluid plus the constant temperature difference between the fluids, we get

$$Ah\Delta T = c_P I_m\left(T_{h1} - \left(T_{c2} + \Delta T\right)\right)$$

which can be transformed to yield

$$\Delta T = \frac{1}{1 + \dfrac{Ah}{c_P I_m}}\left(T_{h1} - T_{c2}\right) = \frac{1}{1 + NTU}\left(T_{h1} - T_{c2}\right) \tag{14.43}$$

Remember that ΔT is the mean temperature difference ΔT_m in our case. Since the temperatures in this equation are those of the fluids at their respective inlets, the temperature difference can be calculated. If we apply the definition of the effectiveness according to Equ.(14.33), we find that

$$\varepsilon = \frac{Ah\Delta T}{\left(Ah + c_P I_m\right)\Delta T} = \frac{NTU}{1 + NTU}$$

which is the result presented in Equ.(14.36). Now, since the temperature difference is constant, the temperature of the first fluid stream is easily calculated from the differential equation

$$c_P I_m \frac{dT_h}{dx} + W\, h\Delta T = 0$$

Using the result for this difference, we find that

$$T_h(x) = T_{h1} - \varepsilon \frac{T_{h1} - T_{c2}}{L} x \tag{14.44}$$

where L is the length of the heat exchanger duct. This shows that the fluid temperatures are linear functions of position for the example of the balanced counter-flow heat exchanger.

14.3.5 The Rate of Entropy Production

Heat exchangers produce entropy as a matter of fact; the reversible exchanger does not exist. Therefore, it is imperative to quantify the magnitude of the irreversibility of heat transfer in such devices. Here, we will derive the expression for the rate of entropy production in a balanced counter-flow heat exchanger for negligible pressure drop of incompressible fluids in the ducts.

A look at the left side of Fig. 14.6 shows that the only fluxes of entropy with respect to the heat exchanger are the four convective currents associated with fluid flow. In steady-state operation, the law of balance of entropy takes the form

$$\Pi_S = \left(s_{h2} - s_{h1}\right)\left|I_{mh}\right| + \left(s_{c1} - s_{c2}\right)\left|I_{mc}\right| \tag{14.45}$$

where s is the specific entropy of the fluid. (Remember that currents leading into the system are counted as negative quantities.) In the case of a fluid having a constant temperature coefficient of enthalpy, the specific entropy is

$$s(T) = s_o + c_P \ln\left(\frac{T}{T_o}\right)$$

which yields the expression for the rate of production of entropy

$$\Pi_S = c_P I_m \ln\left(\frac{T_{h2} T_{c1}}{T_{h1} T_{c2}}\right) = c_P I_m \ln\left(\frac{\left(T_{c2} + \Delta T\right)\left(T_{h1} - \Delta T\right)}{T_{h1} T_{c2}}\right)$$

Since the temperature difference is related to the effectiveness of the heat exchanger according to

$$\Delta T = (1 - \varepsilon)\left(T_{h1} - T_{c2}\right)$$

we can write

$$\begin{aligned}\Pi_S &= c_P I_m \ln\left[\left(1 + \frac{\Delta T}{T_{c2}}\right)\left(1 - \frac{\Delta T}{T_{h1}}\right)\right] \\ &= c_P I_m \ln\left[\left(1 + (1 - \varepsilon)\left(\frac{T_{h1}}{T_{c2}} - 1\right)\right)\left(1 - (1 - \varepsilon)\left(1 - \frac{T_{c2}}{T_{h1}}\right)\right)\right]\end{aligned} \tag{14.46}$$

You can tell very easily from this relation that the rate of production of entropy vanishes for both ideal heat exchangers ($\varepsilon = 1$) and for those with $\varepsilon = 0$. For intermediate values, there is a maximum of entropy production. While the first of these results is to be expected, the latter appears to be paradoxical. However, it can be understood of we realize that the condition $\varepsilon \to 0$ means that the exchanger lets less and less heat pass from the hotter to the cooler fluid. Therefore it represents a vanishing heat exchanger,[8] which certainly does not produce any entropy. This problem demonstrates that we cannot analyze heat exchangers without pressure drop by themselves if we wish to find optimal solutions for the design of a thermal system. The difficulty is resolved with ease, if the effect of the heat exchanger upon an entire system is considered. It is then found that the irreversibility of the total system decreases monotonically with increasing effectiveness of the heat exchanger. If we consider both heat transfer irreversibility and fluid flow irreversibility, however, there are optimal designs for the heat exchangers alone.

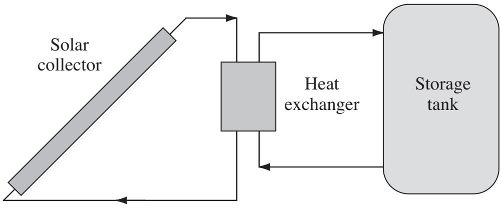
QUESTIONS

10. Why is an ideal heat exchanger necessarily dissipative? What, then, does "ideal" mean?
11. Which parameter has to be adjusted (and how) to make a heat exchanger more effective?
12. Why is a counterflow heat exchanger better than a parallel flow exchanger if viewed from the perspective of dissipation?
13. Why should we consider fluid flow irreversibility along with dissipation due to entropy transfer if we wish to find minimal entropy production rates for a heat exchanger?

EXAMPLE 14.4. Heat exchanger in a solar hot water system.

Consider a simple solar hot water heater with a collector, a balanced counter-flow heat exchanger, and a hot water tank. On the collector side, the fluid is a mixture of water and glycol with a value for the temperature coefficient of enthalpy of 3800 J/(K·kg) and a mass flux of 0.10 kg/s. On the storage side, the fluid is water.

(a) Calculate the flux of mass necessary on the storage side if the heat exchanger is to operate in balanced mode. (b) With an average heat transfer coefficient of 1000 W/(K·m^2) from fluid to fluid, how large should the exchanger surface area be if we wish to have a heat exchanger effectiveness of 90%? (c) It is found that the temperature of the water leaving the storage tank is 20°C, while the temperature of the water-glycol mixture leaving the collector is 80°C. Calculate the temperature of the water entering the storage tank, and the value of the energy current transferred. (d) Could you just as well let the heat exchanger operate in parallel-flow mode?



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[8] See Bejan (1988), p. 614–634, for a comprehensive discussion of heat exchanger irreversibilities (including those associated with friction).

SOLUTION: (a) Since the heat exchanger is to be operated in balanced mode, the two capacitance flow rates are equal. Therefore we have

$$c_{P,coll}I_{m,coll} = c_{P,storage}I_{m,storage} \quad \Rightarrow$$

$$I_{m,storage} = \frac{c_{P,coll}}{c_{P,storage}}I_{m,coll} = \frac{3800}{4200}I_{m,coll} = 0.090\,\mathrm{kg/s}$$

(b) The effectiveness of the balanced counter-flow heat exchanger is given in Equation (222). With the definition of *NTU*, we obtain

$$\begin{aligned}
NTU &= \frac{Ah}{c_P I_m}\\
\varepsilon &= \frac{NTU}{1+NTU} = \frac{Ah/c_P I_m}{1+Ah/c_P I_m} = \frac{Ah}{c_P I_m + Ah}\\
&\Rightarrow \quad (c_P I_m + Ah)\varepsilon = Ah \quad \Rightarrow \quad Ah(1-\varepsilon) = \varepsilon c_P I_m\\
&\Rightarrow \quad A = \frac{\varepsilon c_P I_m}{h(1-\varepsilon)} = \frac{0.9\cdot 3800\cdot 0.10}{1000(1-0.9)}\mathrm{m}^2 = 3.42\,\mathrm{m}^2
\end{aligned}$$

(c) The current of energy transferred between the fluids can be calculated using the definition of the effectiveness in Equ.(14.33):

$$I_E = \varepsilon c_P I_m (T_{h1} - T_{c2})$$

Since the effectiveness and the inlet temperatures of the two fluid streams are known, we find that an energy current equal to

$$I_E = 0.9\cdot 3800\cdot 0.10(80-20)\,\mathrm{W} = 20.5\,\mathrm{kW}$$

is transferred from the collector loop to the storage loop. (This is a fairly large energy flux for a solar hot water system; these conditions can be achieved on a good day with some 40 – 50 m^2 of collector surface area. This result puts the surface area needed for the heat exchanger into perspective.) With this value known, we can compute the outlet temperatures of the two fluid streams:

$$I_E = (c_P I_m)_h (T_{h1} - T_{h2}) \quad \Rightarrow \quad T_{h2} = T_{h1} - \frac{I_E}{(c_P I_m)_h} = 80°\mathrm{C} - 54°\mathrm{C} = 26°\mathrm{C}$$

$$I_E = (c_P I_m)_c (T_{c1} - T_{c2}) \quad \Rightarrow \quad T_{c1} = T_{c2} + \frac{I_E}{(c_P I_m)_c} = 20°\mathrm{C} + 54°\mathrm{C} = 74°\mathrm{C}$$

(d) With an effectiveness of 0.90 for the balanced counter-flow heat exchanger, the value of *NTU* is 9. Using this number also for the operation in parallel-flow mode, Equ.(14.37) yields an effectiveness of 0.50, which is considerably less than the value of 0.90 in counter-flow.

EXAMPLE 14.5. Entropy production in an air-to air heat exchanger with friction.

Write the law of balance of entropy for steady-state operation of an air-to-air heat balanced counter-flow heat exchanger. Give the result for the limiting case of high effectiveness and low pressure drops.

SOLUTION: In this example, we need to know the specific entropy of air entering and leaving the heat exchanger. Since we wish to include the effects of changes of temperature and of pressure, we should give the specific entropy in terms of these two variables. If the air is modeled as an ideal gas, the specific entropy is given by

$$s(T,P) = s_{ref} + c_P \ln\left(\frac{T}{T_{ref}}\right) - \frac{R}{M_0}\ln\left(\frac{P}{P_{ref}}\right)$$

See Chapter 5. In the steady state, the rate of production of entropy is equal to the sum of the four convective fluxes of entropy; this yields

$$\begin{aligned}\Pi_S &= \left(s_{h2} - s_{h1}\right)\left|I_{mh}\right| + \left(s_{c1} - s_{c2}\right)\left|I_{mc}\right| \\ &= c_P I_m \ln\left(\frac{T_{h2}T_{c1}}{T_{h1}T_{c2}}\right) - \frac{R}{M_o} I_m \ln\left(\frac{P_{h2}P_{c1}}{P_{h1}P_{c2}}\right)\end{aligned}$$

The first term was derived in Equ.(14.46). This part of the expression therefore becomes

$$\begin{aligned}\Pi_{S,T} &= c_P I_m \ln\left[\left(1 + (1-\varepsilon)\left(\frac{T_{h1}}{T_{c2}} - 1\right)\right)\left(1 - (1-\varepsilon)\left(1 - \frac{T_{c2}}{T_{h1}}\right)\right)\right] \\ &\approx c_P I_m \ln\left[1 + (1-\varepsilon)\left(\frac{T_{h1}}{T_{c2}} - 1\right) - (1-\varepsilon)\left(1 - \frac{T_{c2}}{T_{h1}}\right)\right]\end{aligned}$$

if we set $1 - \varepsilon \ll 1$, which should hold for large values of the effectiveness. Further modification of the term leads to

$$\begin{aligned}\Pi_{S,T} &= c_P I_m \ln\left[1 - 2(1-\varepsilon) + (1-\varepsilon)\frac{T_{h1}^2 + T_{c2}^2}{T_{h1}T_{c2}}\right] \\ &= c_P I_m \ln\left[1 + (1-\varepsilon)\frac{\left(T_{h1} - T_{c2}\right)^2}{T_{h1}T_{c2}}\right] \approx c_P I_m (1-\varepsilon)\frac{\left(T_{h1} - T_{c2}\right)^2}{T_{h1}T_{c2}}\end{aligned}$$

The pressure term leads to the following contribution to the rate of production of entropy:

$$\Pi_{S,P} = -\frac{R}{M_0} I_m \ln\left(\frac{\left(P_{h1} - \left|\Delta P_h\right|\right)\left(P_{c2} - \left|\Delta P_c\right|\right)}{P_{h1}P_{c2}}\right) \approx \frac{R}{M_0} I_m \left[\frac{\left|\Delta P_h\right|}{P_{h1}} + \frac{\left|\Delta P_c\right|}{P_{c2}}\right]$$

where the last step is a consequence of the assumption that the pressure drops are small compared to the absolute values of the pressure of the fluids.

14.4 STABILITY IN FREE CONVECTION

Sometimes it is not a pump which drives fluid motion in convective heat transfer. In the presence of a gravitational field, convection may take place as a result of buoyancy effects. This phenomenon is well known from boiling water, or from vertical motion of air in the Earth's atmosphere. The latter problem attracted a lot of attention more than 100 years ago when Kelvin tried to calculate the temperature gradient in the atmosphere. Later, it was recognized that this type of convection is responsible, under certain circumstances, for heat transfer inside stars. Here we will discuss the question of how free convection takes place in an atmosphere of an ideal gas.

The condition of convective stability. First we have to answer the question of when free convection occurs. The fluid may be at rest, in which case heat is transported conductively or radiatively. Therefore, there must be special conditions which lead to the onset of convective motion, i.e., to *convective instability*. To find the condition of stability, consider the following model (Fig. 14.8). A fluid parcel is somehow displaced upward from its normal environment. Before the displacement, the values of density, pressure, and temperature inside the parcel are the same as those of its surroundings. The fluid will expand at its new position to adjust its pressure to the new value. As a consequence, the density will decrease. If the new density inside the parcel is larger than that of the surroundings in the upper position, i.e., if

$$\rho_{new} > \rho_2 \tag{14.47}$$

the displaced mass will sink back to its initial position. In this case the fluid layer is stable against convection, and Equ.(14.47) is said to be the *criterion of convective stability*. If Equ.(14.47) is not satisfied, the layer is unstable and the parcel will keep moving since it is less dense than the environment; convection will start to take over.

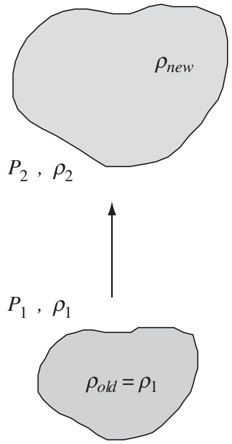

Figure 14.8: A blob of fluid rising in an atmosphere in a gravitational field. It is assumed to expand adiabatically over the distance it travels. If its density is greater than that of the surroundings at its new position, it will sink back down: convective motions will die out. The layer is said to be stable against convection.

We will be able to say more about the new density of the fluid parcel only if we know more about the conditions satisfied during the expansion. Assume convective motion to take place fast enough for *adiabatic conditions* to prevail. As a result, the blob of matter rising upward does not exchange heat with its environment. Only at the end, i.e., when the parcel has risen to the top of the convective layer, does it emit heat to the cooler surroundings. Since the expansion of the blob of ideal gas takes place adiabatically, we can compute the new density according to the Laplace-Poisson law of adiabatic change:

$$\rho_{new} = \rho_{old}\left(\frac{P_2}{P_1}\right)^{1/\gamma} \tag{14.48}$$

Here, P_1 and P_2 refer to the pressure in the lower and the upper positions, respectively. The values are the same inside the blob and the surroundings at any moment. The old density is the same inside the parcel and outside in the lower position. If we apply the law of adiabatic change to a small vertical displacement we can write the pressure and the density at the upper position in terms of the values at the lower point. With

$$P_2 = P_1 + \frac{dP}{dz}\Delta z$$

and

$$\rho_2 = \rho_1 + \frac{d\rho}{dz}\Delta z$$

we transform the stability criterion of Equ.(14.47) to

$$\frac{1}{P}\frac{dP}{dz} > \gamma\frac{1}{\rho}\frac{d\rho}{dz} \tag{14.49}$$

It is convenient to express this condition in terms of the temperature gradient *dT/dz*. Since for the ideal gas

$$\frac{1}{\rho}\frac{d\rho}{dz} = \frac{1}{P}\frac{dP}{dz} - \frac{1}{T}\frac{dT}{dz}$$

the final form of the stability criterion is the following:

$$\frac{dT}{dz} > \left(1 - \frac{1}{\gamma}\right)\frac{T}{P}\frac{dP}{dz} \tag{14.50}$$

According to Example 5.6, the quantity on the right-hand side is the adiabatic temperature gradient. Since both the pressure and temperature gradients are negative quantities, the criterion expresses the following result: *If the magnitude of the actual temperature gradient dT/dz is smaller than the magnitude of the adiabatic temperature gradient, the fluid layer is stable against convective motion.*

14.4.1 Calculating the Energy Flux Due to Convection

Which value will the temperature gradient take if convection is responsible for the transport of heat? According to Equ.(14.50), all we know is that its magnitude will be greater than the magnitude of the adiabatic gradient. The excess of the actual gradient over the adiabatic gradient is responsible for the magnitude of the net convective flux of heat or energy:

$$j_{E,conv} = \left(\left.\frac{dT}{dz}\right|_{ad} - \frac{dT}{dz}\right)\Delta z c_P \rho v = \Delta\nabla T\, \Delta z c_P \rho v \tag{14.51}$$

Here, Δz is the average distance travelled by the moving blobs, while c_P is the specific temperature coefficient of enthalpy of the gas; v is the average velocity of the parcels. The excess of the temperature gradient over the adiabatic one has been abbreviated by $\Delta\nabla T$. Note that we have neglected the kinetic energy term in Equ.(14.51). In practice, it may be very difficult to compute the actual temperature gradient. There are some cases, however, in which the excess is extremely small, and the gradient is very nearly the adiabatic one (Problem 16).

In Equ.(14.51), the average distance travelled by the blobs of air plays a central role. There is a particular approach to calculating this quantity called the *mixing length approximation*. Assume the parcels of matter rising in free convection to be carried over an average distance which is called the mixing length l_{mix}. If we assume gradients to be constant over the mixing length, we can develop an approximation for the net energy flux carried over this distance. However, we still need an expression for the average velocity of the parcels in that equation. The velocity attained by a parcel is a consequence of the acceleration due to buoyancy. According to Equ.(14.49), the excess of density $\Delta\rho_{ex}$ for a distance Δz is equal to

$$\Delta\rho_{ex} = \left(\frac{d\rho}{dz} - \frac{1}{\gamma}\frac{\rho}{P}\frac{dP}{dz}\right)\Delta z = \frac{\rho}{T}\Delta\nabla T\, \Delta z$$

where $\Delta\nabla T$ is the excess of temperature for the same distance which appears in Equation (237). Half of this density excess multiplied by the gravitational field strength g is the average net force per volume over the distance Δz. If we multiply this quantity by the distance Δz, we obtain the kinetic energy per volume gained by the parcel:

$$\frac{1}{2}\rho v_f^2 = \frac{1}{2} g\left(\frac{\rho}{T}\Delta\nabla T\, \Delta z\right)\Delta z$$

v_f is the final velocity of the blob, which we take to be twice the average value. This equation allows us to eliminate the flow speed from the expression for the net energy flux. Using the mixing length l_{mix} for the distance Δz, we obtain the following expression for the energy flux density:

$$j_{E,conv} = \frac{1}{2} c_P \rho \left(\frac{g}{T} \right)^{1/2} \Delta \nabla T^{3/2} l_{mix}^2 \tag{14.52}$$

EXERCISES AND PROBLEMS

1. Consider laminar flow over a flat plate. Show that the heat transfer coefficient increases as the square root of the velocity of the free stream. Also show that the average heat transfer coefficient over a length L of the plate is equal to twice its local value at L. How do you derive the entropy transfer coefficient from this result?
2. Consider a pebble bed through which air is pumped. (Pebble bed heat storage is one of the means of storing energy from the sun for heating purposes.) Show that in the purely one-dimensional case the differential equations for the temperature of the air and of the pebbles as a function of time and of axial position are given by

$$\left(\rho c_P\right)_a e \frac{\partial T_a}{\partial t} = -\frac{1}{A}\left(c_P I_m\right)_a \frac{\partial T_a}{\partial x} - h^*\left(T_a - T_p\right)$$

$$\left(\rho c_P\right)_p (1-e) \frac{\partial T_p}{\partial t} = h^*\left(T_a - T_p\right)$$

   Here, A is the cross section of the pebble bed, while e denotes the bed void fraction. h^* is the heat transfer coefficient between air and pebbles multiplied by the pebble surface per unit bed volume. The following additional assumptions have been made: no heat loss to the environment and no temperature gradient within the pebbles.
3. If you include in the balance of energy, the energy delivered by the pump to maintain the pressure of the air in an solar air collector, how does the form of the equation of balance of entropy in Equ.(14.29) change?
4. Express the law of balance of entropy for a flat-plate solar collector in steady-state operation. Do this for uniform models and for models where the temperature of the fluid (and of the absorber) change in the direction of flow.
5. A fluid is flowing through a pipe which is being heated from outside. (This setup can be found in line focus concentrators for solar radiation.) Show that the differential equation for the temperature of the fluid as a function of position in the direction of flow is given by

$$c_p I_m \frac{dT}{dx} = F'\left[\sigma_E - 2\pi r_o U_L \left(T - T_a\right)\right]$$

   where

$$F' = \frac{1/U_L}{1/U_{fa}}$$

   can be called the efficiency factor of the tubular heater. U_L is the heat loss coefficient from the pipe to the surroundings (see Problem 12 of Chapter 7 for a numerical example) while U_{fa}, which represents the heat transfer coefficient from the fluid to the environment, was calculated in Problem 12 of Chapter 7. σ_E is the rate of absorption of energy per length of pipe, and T_a is the ambient temperature.

6. In Problem 5, assume F' and U_L to be constant. Show that the convective energy flux which is carried away by the fluid in the heated pipe can be expressed by

$$I_{E,useful} = F_R L\left[\sigma_E - 2\pi r_o U_L\left(T_{f,in} - T_a\right)\right]$$

where

$$F_R = \frac{c_p I_m}{2\pi r_o L U_L}\left[1 - \exp\left(-\frac{2\pi r_o L U_L F'}{c_p I_m}\right)\right]$$

is called the heat removal factor for the pipe of length L. $T_{f,in}$ is the inlet temperature of the fluid. Note that the result is similar in structure to the one obtained for flat-plate solar collectors (Section 14.2).

7. Consider a parabolic trough concentrator for solar light with a metal pipe running along the line focus. A fluid is pumped through the pipe. Take the concentration factor of the radiation to be C, and give the pipe a radius r and a length L. (a) If you neglect convective losses and if the heat transfer coefficient from the surface of the pipe absorbing sunlight to the fluid is very large, show that the differential equation for the temperature of the fluid in the direction of flow is

$$c_p I_m \frac{dT}{dx} = 2r\left[C(\tau\alpha)\mathcal{G}_b - \pi e\sigma\left(T^4 - T_a^4\right)\right]$$

Here it has been assumed that all the light falling onto the mirrors (expressed in terms of direct solar irradiance $\mathcal{G}_b$, i.e., the irradiance excluding diffuse light) is concentrated onto the projection area of the pipe, and that a fraction $(\tau\alpha)$ of the incoming radiation is absorbed. The factor e is the emissivity of the pipe. (b) Calculate the exit temperature of the fluid for given operating conditions and for inlet temperature $T_{f,in}$.

8. The analysis of the solar air collector of Section 9.4 can be repeated for different heights of the air duct. Changing this parameter changes the location of the minimum of the rate of production of entropy. It is found that the minima for different heights are approximately found for collector lengths which leave the cross section of the duct constant. Can you explain this behavior?

9. Derive the equations for the effectiveness of counter-flow and parallel-flow heat exchangers (Equ.(14.34) and Equ.(14.37)).

10. Compare balanced counter-flow and parallel-flow heat exchangers, both with an *NTU* of 5. Which of the exchangers has the higher effectiveness?

11. Compare balanced and unbalanced counter-flow heat exchangers. If they are built identically, do they have the same effectiveness? (To be concrete, take the smaller of the two capacitance flow rates to be equal to the one used in the balanced mode.)

12. Explain in qualitative terms why the effectiveness of a parallel-flow heat exchanger operated in balanced mode cannot be greater than 0.5. (*Hint:* see Fig. 14.7.)

13. For convective motion in the mantle of the Earth it is found that the Grüneisen ratio γ^* (defined in Problem 7 of the Chapter 10) is not constant, but varies inversely as the density of the material.[9] Show that, in this case, the solution of the differential equation of adiabatic motion can be written as follows:

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[9] See Stacey(1992), p. 305 and appendixes therein.

$$\frac{T_1}{T_2} = \exp\left[\gamma_1 * \left(\frac{\rho_1}{\rho_2} - 1\right)\right]$$

14. Show that the adiabatic temperature gradient of a fluid in hydrostatic equilibrium can be expressed by

$$\left.\frac{dT}{dz}\right|_{ad} = -\frac{T\alpha_V g}{c_p} \quad \text{or} \quad \left.\frac{dT}{dz}\right|_{ad} = -\gamma * T\rho g\kappa_s$$

Again, γ^* is the Grüneisen ratio defined in Problem 7 of the Chapter 10.

15. As we have found before in examples in Chapter 7, the entropy generated in the Earth's interior cannot be transported by conduction because this mode of heat transfer is not effective enough under the given circumstances. It is therefore assumed that heat must be transferred convectively, and the material of the mantle is modeled as an ideal fluid as discussed in the Interlude. Make a model of convective motion of the Earth's mantle in which a blob of matter rises adiabatically from the interior to the surface (as in the model for the Earth's atmosphere in Section 9.6, or as discussed in Section 14.4). (a) Assume that the heating at a given radius is due to entropy production as the result of radioactive decay (which is assumed to be distributed evenly over the entire mantle) at smaller radii, and friction which assumes all the energy released by the heat engine represented by the convective motion to be dissipated whereby more entropy is returned to the rising matter. Show that in this case, the entropy current entering a thin shell at radius r and driving the heat engine is given by

$$I_s(r) = \frac{1}{T(r)}\frac{m(r) - m(r_c)}{m(R) - m(r_c)} I_E(R)$$

where r_c and R are the radius of the core (bordering on the mantle) and the radius of the Earth, respectively. $I_E(R)$ is the energy flux penetrating the Earth's surface from the interior of the planet. (b) It is found that the gravitational field g is roughly constant in the entire mantle. Show that in this case

$$I_s(r) = \frac{1}{T(r)}\frac{r^2 - r_c^2}{R^2 - r_c^2} I_E(R)$$

(c) Show that if you assume the temperature gradient through the mantle to be adiabatic, it can be expressed by

$$\mathcal{P} \approx g I_E(R) \int_{r_c}^{R} \frac{r^2 - r_c^2}{R^2 - r_c^2} \gamma * \rho\kappa_s dr$$

where γ^* is the Grüneisen ratio defined in Problem 7 of the Chapter 10, and κ_s is the adiabatic compressibility of the material. (*Hint:* See Problem 14.) (d) The values of the different physical parameter of the Earth's interior have to be derived from seismic and other measurements.[10] Take an average density of 4500 kg/m^3, and average values of 10 N/kg, 0.8, and $3 \cdot 10^{-12}$ /Pa for the gravitational field, the Grüneisen ratio, and the adiabatic compressibility, respectively. The lower boundary of the mantle is at 3500 km from the center of the Earth, and the energy flux through the surface is $31 \cdot 10^{12}$ W. Estimate the efficiency of the convective motion interpreted as a heat engine.

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[10] See Stacey (1992) for numerical values for the Earth's interior.

16. Estimate the amount by which the actual temperature gradient inside a massive main sequence star surpasses the adiabatic gradient. In a star of about 5 solar masses (which makes it 10^{31} kg) heat is carried by convection in the innermost parts, and by radiation further out. The energy flux not too close to the center may be taken to be the total flux of $2.4 \cdot 10^{30}$ W (which is about three to four orders of magnitude larger than the luminosity of the Sun). The radius of such a star is $1.75 \cdot 10^{9}$ m, and its central temperature has a value of some 27 million K. (The values reported here are the result of numerical modeling.) Would you say that convection inside such a star follows the assumption that heat is not exchanged during upward (and downward) motion of the blobs?

CHAPTER 15

PHASE CHANGE, MIXTURES, AND ENGINES

In this chapter, I will go more deeply into some phenomena having to do with phase change and mixtures of gases such as moist air. These will lead to important applications in engineering and the natural sciences. First, there will be a description of phase change that makes use of concepts developed in the previous chapters. Then I turn to mixtures of two phase fluids such as moist air which will allow me to briefly discuss evaporation. Simple models of vapor power and refrigeration cycles will conclude this chapter.

15.1 PHASE CHANGES IN SIMPLE FLUIDS

In Chapter 5, phase change of simple fluids was discussed from the viewpoint of the entropy needed to melt or vaporize a substance. Then, in Chapter 6, the phenomenon was described as a chemical reaction. This led to explanations of the change of melting or boiling points, and vapor pressure. The chemical viewpoint prepares us for the discussion of the entropy necessary for phase changes, vapor pressure and Clapeyron's law, and property tables.

15.1.1 A Description of Phase Changes

Here, we will describe in more concrete terms what happens to a fluid as a consequence of fusion, vaporization, or sublimation. So that we will not always have to mention all three processes, we will usually choose one of them as an example. We will see how much entropy and energy are involved in a phase change, and we will discover that there exist clear relations between the temperature and the pressure at the transition. In Chapter 4 and 5, we described the melting or the vaporization of a body using the *TS* diagram of the process, a tool which we will use again. We will begin by describing the processes of vaporization and condensation.

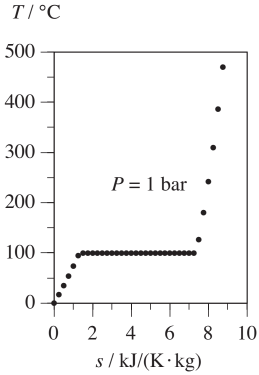

Figure 15.1: For 1 kg of water being heated at constant pressure of 1.0 bar, the temperature rises as a function of the entropy content. The horizontal section of the curve corresponds to the phase during which vaporization takes place: addition of entropy does not change the temperature of the fluid.

Vaporization of water. For the sake of argument, consider 1 kg of water being heated from 0°C at a constant pressure of 1 bar (Fig. 15.1). For water being heated, entropy and temperature rise from values of zero along the section of the curve at the bottom left (for entropy, this is an arbitrary choice). During this phase, water is said to be a *compressed (subcooled) liquid*. Since water is nearly incompressible, the relation is approximated by the one derived in Chapter 4 (Equ.(4.42)):

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_16,

$$s(T) = s(T_0) + c_P \ln\left(\frac{T}{T_0}\right) \tag{15.1}$$

This agrees well with what can be read from Fig. 15.1. (Remember that c_P for water is about 4200 J/(kg·K).) At a temperature of 100°C, the water begins to boil. Just before the onset of boiling, the fluid is said to be a *saturated liquid*. While the entropy of the fluid increases, the temperature stays constant: the curve cuts horizontally through the *TS* diagram at the temperature of vaporization. During this part of the process, the fluid is a *mixture of liquid and vapor*. Finally, when all the water has been turned into steam, the temperature of the vapor begins to rise again as its entropy increases. Again, there is a name for the fluid just after the point when all of it has turned into gas: it is called a *saturated vapor*. When heated, pure vapor (without any liquid left) is said to be *superheated water vapor*. Equ.(15.1) can be accepted as an approximation for the actual relation between temperature and entropy for the gas as well, if we take steam as an ideal gas having a constant temperature coefficient of enthalpy, see Chapter 5. (According to Fig. 15.1, the average value of c_P between 100°C and 200°C is around 2000 J/(kg·K).)

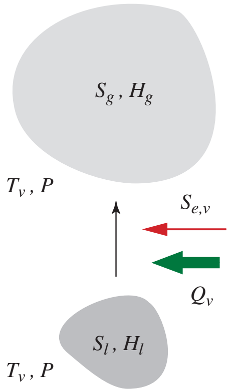

Figure 15.2: A certain amount of a liquid vaporizes. The entropy added remains in the body, while part of the added energy goes toward expansion. The added energy is equal to the change of enthalpy of the fluid body.

Amount of substance, entropy, and energy. Let us take a closer look at the transition and the balance of entropy and energy (Fig. 15.2). Consider the pure liquid at the boiling point. Entropy is added, and a certain amount of the liquid is transformed into vapor. Looked at from the viewpoint of a chemical reaction, we may say that only one substance is involved on either side of the reaction equation

$$\text{A} \rightarrow \text{B}$$

As a consequence, if the change of amount of substance of species A is Δn, then the corresponding change for B is $-\Delta n$:

$$\Delta n_l = -\Delta n_g \tag{15.2}$$

The subscripts *l* and *g* indicate the liquid and vapor (gaseous) phases, respectively. In terms of the change of the amount of substance of the vapor, the entropy necessary for vaporization can be written as follows:

$$S_{e,v} = \bar{l}_v \Delta n_g \tag{15.3}$$

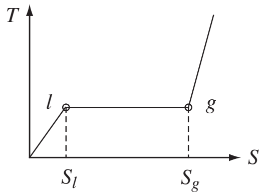

Figure 15.3: The entropy of vaporization can be read from the *TS* diagram, where the value corresponds to the length of the horizontal section of the curve. Points *l* and *g* denote the states of saturated liquid and of saturated vapor (gas).

Observation tells us that vaporization at constant pressure and temperature proceeds reversibly. This means that the entropy added to the liquid phase will be present in the vapor phase (Fig. 15.3). The *latent entropy l* of the phase change can therefore be expressed in terms of the entropies of the liquid and the gas:

$$\bar{l}_v = \bar{s}_g - \bar{s}_l \tag{15.4}$$

The phase change is also described in terms of the energy exchanged (see Fig. 15.2). Since the process takes place at constant temperature, the energy added for vaporization is the product of T_v and $S_{e,v}$ as expressed by Equ.(15.3). If we remember that the phase change also takes place at constant pressure, we can conclude that the energy added in heating is equal to the change of enthalpy of the fluid, see Chapter 5. Part of the energy is used to raise the internal energy, while the rest is emitted because of the expansion of the fluid. In summary, the change of entropy and the change of enthalpy (the latent enthalpy of vaporization) are related by

$$\bar{h}_g - \bar{h}_l = T_v\left(\bar{s}_g - \bar{s}_l\right) \tag{15.5}$$

Naturally, these relations can also be expressed on the basis of mass rather than amount of substance. We simply introduce the specific entropy of vaporization l_v and relate it to the difference of the specific entropies of the fluid in the liquid and the vapor phases. Then, in Equ.(15.5), we have the specific enthalpy and the specific entropy. The latent enthalpy of vaporization is sometimes abbreviated by Δh_v.

Vaporization at different pressures. From experience we know that water boils at different temperatures depending upon the pressure of the fluid. If the pressure is lower than 1 bar, the boiling point is also lower. Since the change in pressure hardly affects the properties of liquid water, we expect a *TS* diagram of the process of heating to start off just as in the lower left of the curve in Fig. 15.1. Then, however, the curve must break off at an earlier point and cut across the diagram horizontally. Measurements show that more entropy is needed to vaporize the same amount of water at lower pressure. Finally, when all the water has turned into steam, the temperature continues to climb again. For higher pressures, the changes with respect to the case of 1 bar are just the opposite. If the *TS* curves for different values of the pressure are drawn in the same diagram, we get the result shown in Fig. 15.4. The amount of energy necessary for vaporization depends not only upon the amount of entropy needed, but also upon the temperature of vaporization. It turns out the amount of energy necessary for vaporization decreases with increasing pressure.

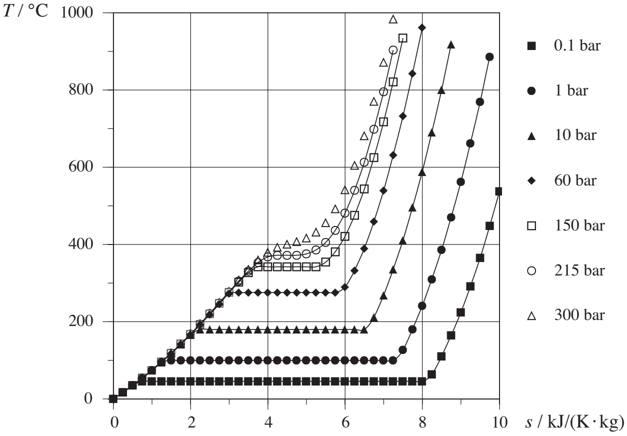

Figure 15.4: *TS* diagram for 1 kg of water heated from 0°C at constant pressure. The curves are for different values of pressure, ranging from 0.1 bar to 300 bar. The last set of points shows that when the pressure is larger than the critical pressure of 220 bar, the vapor does not condense any more. The values were computed using the Steam-NBS function implemented in the program EES (Klein et.al, 1991).

There are some interesting points to note. The horizontal sections of the *TS* curves, i.e., those parts which display the process of vaporization, form a bell-shaped area on the *TS* diagram (Fig. 15.5). The diagram can be divided into three sections, one on the left of the bell for the *compressed liquid phase*; one to the right, for the *superheated vapor*; and the bell area itself, where *mixtures of liquid and vapor* are present. The liquid phase basically occupies only a very thin strip along the saturated liquid line; this is because the properties of liquid water do not depend strongly upon pressure. Only for very large pressures, of the order of hundreds or thousands of bar, do the properties of water differ considerably from the saturated state. The curve bounding the bell is divided into two parts; the left denotes the states of *saturated liquid* (pure liquid just at the verge of vaporization), and the right shows the states of *saturated vapor* (pure vapor on the verge of condensation). The two sections meet at the top of the bell, at a point called the *critical point*. If you have water vapor at pressures above the critical pressure of 220.9 bar, and you cool the vapor at constant pressure, it will no longer condense. Rather, as you can see in Fig. 15.4, the temperature will pass above the critical temperature of 374.14°C for values of the specific entropy of 4.43 J/(K·kg).

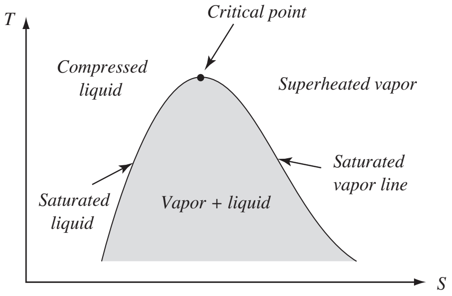

Figure 15.5: The line for saturated fluid (liquid and vapor) is shown in the *TS* diagram. The dome shaped area below the line is occupied by the mixed phase of liquid and vapor. The line separates this area from those of the compressed liquid and the superheated steam.

The pressure-temperature relation for boiling. Obviously, there is a relation between the boiling point, i.e., the temperature of vaporization, and the pressure at which the transition takes place. As Fig. 15.4 demonstrates, the higher the pressure, the higher the temperature. Such a relation is rather different from what we know about liquids or gases. With incompressible liquids, the properties depend only upon the temperature, and the pressure does not come into play. For gases, on the other hand, two independent properties define the temperature; one variable, such as the pressure, is not enough. For this reason, the relation between temperature and pressure at vaporization is remarkable. A typical pressure-temperature curve for a fluid appears in Fig. 15.6. Note that the line has a beginning and an end. The end we already know: it is the critical point of the fluid. The beginning of the line, however, will be understood shortly, when we transfer our description to the other two phase transitions as well. The beginning point is called the *triple point* of the substance.

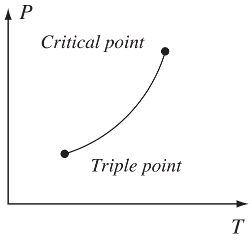

Figure 15.6: At vaporization, pressure and temperature of the fluid are directly related. *P* is called the vapor pressure at *T*.

Pressure-temperature relations for all three phase transitions. Most of the observations made about vaporization can be transferred to melting and sublimation (the direct transition between solid and vapor). Specific amounts of entropy are needed for these transformations (or are emitted for the reverse processes); the energy required is related to this quantity by the temperature of the phase transitions. While the process runs at constant pressure, the temperature stays constant. In each case, the pressure is only dependent upon the temperature during the change.

Take the case of water freezing or ice melting. Even though it is harder to observe, changes of pressure affect the melting point; the reason for the difficulty lies in the fact that the pressure-temperature curve for melting is very steep (Fig. 15.7). On the other hand, this effect leads to the phenomenon of freezing water being able to split rocks: water freezing at temperatures only slightly below 0°C develops a tremendous pressure. Having observed this, we have to conclude that the pressure-temperature relation for melting has a negative slope, unlike what we know of the vaporization of water, and, in fact, just about unlike anything else known in nature. Water expands upon freezing, while most other substances contract.

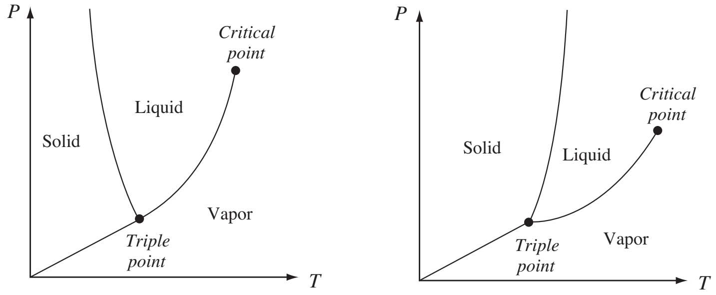

Figure 15.7: Phase diagrams for water (left) and other substances (right) show the pressure-temperature relations of the phase transitions solid-liquid, liquid-vapor, and solid-vapor. At the triple point, which has unique values of pressure and temperature, the three phases coexist. At temperatures (and pressures) above the critical point, liquid and vapor are indistinguishable.

For the third phase transition, sublimation, an analogous pressure-temperature relation exists. The three lines meet in a single point, the so-called triple point, where all three phases coexist. Drawing the three *P(T)* functions leads to the phase diagrams shown in the graphs above.

15.1.2 Phase Transformations and Chemical Equilibrium

Phase changes can be understood in terms of chemical reactions (Chapter 6). If the chemical potential of a phase is higher at given pressure and temperature than that of another phase, the former will change into the latter. The conditions necessary for the changes to occur can therefore be found by considering chemical equilibrium between the phases. This section will show how easily the chemical potential may be used to understand phenomena related to phase transitions.

Melting and vaporization as chemical reactions. Phase changes can be viewed as a particular kind of chemical transformation, subject to the same laws we have studied in Chapter 6, where we were able to calculate what happens as a consequence of a chemical reaction on the basis of the chemical potentials of the substances. Here, the substances are solid (*s*), liquid (*l*), and gaseous water (*g*). If you look at Table 6.2, you see that at standard conditions, liquid water has the lowest chemical potential. This means that we should expect both ice and vapor to change into liquid water at a temperature of 25°C and a pressure of 1 atm.

The values of the temperature coefficients of the chemical potential found in Table 6.2 allow us to compute approximate values for the temperatures of the melting point and the point of vaporization, if the pressure remains constant. Points of phase transitions are obviously those where two phases coexist. If ice becomes liquid at a temperature of 25°C, because under this condition its chemical potential is larger than that of the liquid, we simply ask at which value of the temperature the tendency of water to change into ice has become equally large as the drive of ice to melt. In other words, we want to know the temperature for which the two chemical potentials have become equal:

$$\mu_{ice}\left(T_f, P_0\right) = \mu_{liquid}\left(T_f, P_0\right) \tag{15.6}$$

Since the potentials change with temperature according to Equ.(6.24), the condition expressed in this equation becomes

$$\mu_{ice}^0 + \alpha_{\mu,ice}\left(T - T_0\right) = \mu_{liquid}^0 + \alpha_{\mu,liquid}\left(T - T_0\right) \tag{15.7}$$

Solving this simple equation, we obtain 274.7 K for the melting point of water. Considering that this is just a linear approximation, the result is quite acceptable.

Pressure dependence of the melting point. The problem of the change with pressure of the melting point and the temperature of vaporization is even more interesting, since it involves both changes in pressure and in temperature. Again, the chemical potentials of liquid and solid (or gaseous) water have to be equal at the actual melting point (or point of vaporization), and again the potentials change with temperature, and this time also with pressure. Therefore, the following condition must be satisfied:

$$\begin{aligned}&\mu_{ice}^0 + \alpha_{\mu,ice}\left(T - T_0\right) + \beta_{\mu,ice}\left(P - P_0\right)\\&\qquad = \mu_{liquid}^0 + \alpha_{\mu,liquid}\left(T - T_0\right) + \beta_{\mu,liquid}\left(P - P_0\right)\end{aligned} \tag{15.8}$$

For simplicity, assume the reference temperature to be the value of the melting point T_f at the reference pressure, in which case the standard potentials of ice and water are equal. With this in mind, we arrive at a relation between the change of pressure and temperature:

$$\frac{\Delta P}{\Delta T} = -\frac{\alpha_{\mu,liquid} - \alpha_{\mu,ice}}{\beta_{\mu,liquid} - \beta_{\mu,ice}} \tag{15.9}$$

Using the values for water from Table 6.2, we obtain an interesting result, which is that the melting point of ice decreases with increasing pressure (with the corresponding values at 0°C we get the result of $\Delta P/\Delta T = -\ 135$ bar/K). This is so because the pressure coefficient of ice is larger than that of water, a condition which holds only for water, and maybe one or two other substances. Generally, the temperature of the melting point increases with increasing pressure. The same is true for the temperature of vaporization, which increases if more pressure is applied. This also holds for water: water boils at higher temperature if the pressure is increased (see the discussion about vaporization at different pressures presented below).

In Chapter 8, and again in Chapter 10 (Equations (10.51) and (10.52)), we saw that, at least for the bodies we have studied, the temperature coefficient of the chemical potential is the negative molar entropy of the substance, and the pressure coefficient is the molar volume. Applying this and writing *l* and *s* for liquid and solid, respectively, Equ.(15.9) becomes

$$\frac{\Delta P}{\Delta T} = \frac{\bar{s}_l - \bar{s}_s}{\bar{v}_l - \bar{v}_s} \tag{15.10}$$

This result is of much more general importance than could be guessed from the derivation. It is called *Clapeyron's law*, and it shows that the change of pressure accompanying a change of temperature of phase transformation depends upon the entropy necessary for the phase change and the change of volume of the fluid (remember the formal derivation in Section 10.2.6). Another derivation of this result based on a cyclic process will be presented below. Note that you can apply Equ.(15.10) to vaporization as well. Since the change of volume is much larger in vaporization, the change of pressure with a change of boiling point should be much less dramatic than what we have observed for melting ice.

15.1.3 Vapor Pressure

What is it that makes the states of saturated liquid or vapor special? What is the relation between the pressure of the fluid and the temperature at which it changes its phase? To answer these questions, consider some liquid put into an otherwise empty container. It is easy to see what happens if you place a drop of the liquid at the top of the mercury column in a pressure gauge (Fig. 15.8). Even though the weight of the drop is so small as not to add to the pressure of the column of mercury, the top of the mercury column is observed to go down; obviously, there is some fluid in the previously empty space at the top of the gauge which has a noticeable pressure. We interpret this observation by assuming that a part of the drop has vaporized, and the pressure of the vapor is responsible for the change of height of the mercury column. Naturally, the pressure of the remaining liquid at the top of the gauge is the same as that of the vapor, and this pressure is called the *vapor pressure* of the fluid. It is further observed that the vapor pressure depends only upon the temperature of the fluids involved, as long as there always is at least a little bit of liquid left. How can we understand this relation between the temperature of the fluids and the vapor pressure?

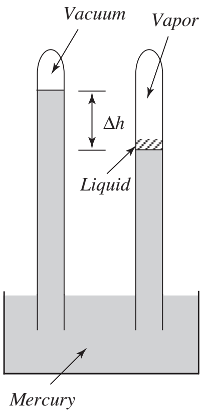

Figure 15.8: Detecting the pressure of the vapor which forms from the liquid at the top of a mercury gauge.

For a given temperature, after the physical variables have assumed constant values, the situation of the fluid and its vapor is that of an insulated system inside a container (Fig. 15.9). Since volume and energy are kept constant, the only possible changes inside the container are the transformation of vapor into liquid (or vice versa), and the production of entropy. According to Equ.(6.34), the entropy production rate equals

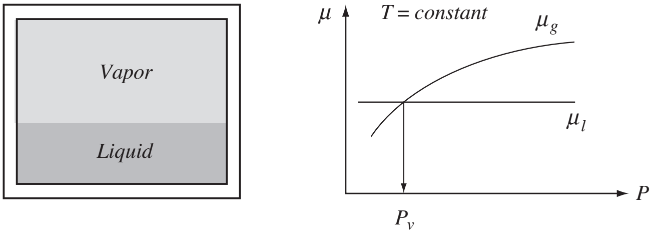

Figure 15.9: The chemical potential of the vapor inside the container changes much more strongly with pressure than the chemical potential of the liquid. Therefore, it is easy to conceive of conditions for which μ_g is either smaller or larger than μ_l. In the latter case, some of the vapor will condense. When the chemical potentials are equal, the phases are in equilibrium.

$$\Pi_S = \frac{1}{T}\left|\mu_g - \mu_l\right|\left|\dot{n}\right| \qquad (15.11)$$

Assume for the moment that the chemical potential of the vapor is larger than that of the liquid. In this case, we expect some of the substance to go from the vapor into the liquid phase. Since this process will stop when equilibrium conditions have been reached, we have to conclude that the chemical potentials of the vapor and of the liquid phase have to be equal in equilibrium; it is equally likely for liquid to change into vapor as it is for vapor to condense:

$$\mu_g(P,T) = \mu_l(P,T) \qquad (15.12)$$

We can estimate the value of the vapor pressure of water at a temperature of 25°C from the values found in Table 6.2. With the temperature given, the values of the chemical potential depend only upon pressure. Since, in Table 6.2, they are given for the standard pressure of 1 atm, we have to change the potentials to the condition of the as yet unknown vapor pressure. If we treat water vapor as an ideal gas, and water as an incompressible fluid, we have

$$\mu_g^0 + RT\ \ln\left(\frac{P_v}{P_0}\right) = \mu_l^0 + \left(P_v - P_o\right)\bar{\upsilon}_{l0} \tag{15.13}$$

as the condition of chemical equilibrium between liquid water and its vapor at 25°C. If you plug in some values, you will notice that the pressure term for the liquid is very small compared to the other terms, which means that the actual pressure of the liquid does not greatly influence the result. (For example, giving the liquid a larger pressure than the value P in the diagram of Fig. 15.9 will shift the horizontal line upward by a very small amount.) The important parameter is the vapor pressure. Solving the condition for the value of P_v yields

$$\ln\left(\frac{P_v}{P_0}\right) = -\frac{1}{RT}\left(\mu_g^0 - \mu_l^0\right) \tag{15.14}$$

(see Fig. 15.10). With the values taken from Table 6.2, the vapor pressure of water at 298 K is estimated to be 3150 Pa. This is close to the measured value of 3169 Pa (see Table 15.1).

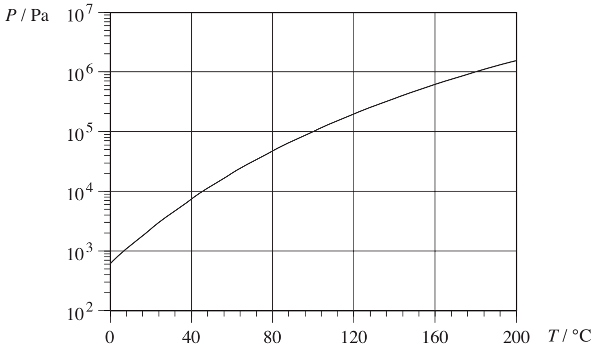

Figure 15.10: With increasing temperature, the vapor pressure of water rises rapidly. The values must be obtained from measurements, since the fluids do not obey simple constitutive relations. Note that, in order to obtain the vapor pressure at a certain temperature from a theoretical correlation such as Equ.(15.14), the chemical potentials have to be also adjusted for the temperature.

Interpreting the condition of equilibrium in Equ.(15.12), we conclude that a particular relation between temperature and pressure exists as long as there is equilibrium between the phases. The pressure of the vapor cannot be changed independently of temperature as in the case of a single phase gas with constant amount of substance. The main difference is that in this case the gas is in equilibrium with its condensate. When the temperature is increased, more vapor is added to the vapor phase; when the temperature is decreased, some of the vapor can change into the liquid phase. This free exchange of amount of substance is responsible for the fact that the vapor pressure of a substance is a unique function of temperature. The answer to the question posed at the beginning of the section can now be given: the points of the bell-shaped curve in

Fig. 15.5 are those for which the chemical potentials are the same at a given temperature. They correspond to the conditions of chemical equilibrium between liquid and vapor.

Table 15.1: Properties of saturated water (liquid–vapor)[a]

T °C	P_v bar	$\mu_l = \mu_g$ kG	s_l kJ/K·kg	s_g kJ/K·kg	υ_l*1000 m^3/kg	υ_g m^3/kg	e_l kJ/kg	e_g kJ/kg
0.01	0.00612	0.000	0.0000	9.1541	1.0002	205.987	0.00	2374.5
5	0.00873	–0.003	0.0763	9.0236	1.0001	147.0239	21.02	2381.4
10	0.01228	–0.014	0.1510	8.8986	1.0003	106.3229	41.99	2388.3
15	0.01706	–0.031	0.2242	8.7792	1.0009	77.8971	62.92	2395.2
20	0.02339	–0.054	0.2962	8.6651	1.0018	57.7777	83.83	2402.0
25	0.03169	–0.084	0.3670	8.5558	1.0030	43.3566	104.75	2408.9
30	0.04246	–0.120	0.4365	8.4513	1.0044	32.8955	125.67	2415.7
35	0.05627	–0.162	0.5050	8.3511	1.0060	25.2204	146.58	2422.5
40	0.07381	–0.211	0.5723	8.2550	1.0079	19.5283	167.50	2429.2
45	0.09590	–0.265	0.6385	8.1629	1.0099	15.2634	188.41	2435.9
50	0.12344	–0.326	0.7037	8.0745	1.0122	12.0367	209.31	2442.6
60	0.19932	–0.464	0.8312	7.9080	1.0171	7.6743	251.13	2455.8
80	0.47373	–0.807	1.0753	7.6112	1.0290	3.4088	334.88	2481.6
100	1.01322	–1.235	1.3069	7.3545	1.0434	1.6736	418.96	2506.1
120	1.98483	–1.743	1.5278	7.1297	1.0603	0.8922	503.57	2529.1
140	3.61195	–2.329	1.7394	6.9302	1.0797	0.5090	588.85	2550.0
160	6.17663	–2.987	1.9429	6.7503	1.1019	0.3071	674.97	2568.3
180	10.01927	–3.714	2.1397	6.5853	1.1273	0.1940	762.12	2583.4
200	15.53650	–4.508	2.3308	6.4312	1.1564	0.1273	850.58	2594.7
220	23.17846	–5.364	2.5175	6.2847	1.1900	0.0862	940.75	2601.6
240	33.44673	–6.281	2.7013	6.1423	1.2292	0.0597	1033.12	2603.1
260	46.89449	–7.256	2.8838	6.0009	1.2758	0.0422	1128.4	2598.4
280	64.13154	–8.287	3.0669	5.8565	1.3324	0.0302	1227.53	2585.7
300	85.83784	–9.371	3.2534	5.7042	1.4037	0.0217	1332.00	2562.8
320	112.79318	–10.506	3.4476	5.5356	1.4984	0.0155	1444.35	2525.2
340	145.94085	–11.691	3.6587	5.3345	1.6373	0.0108	1569.93	2463.9
360	186.55306	–12.924	3.9153	5.0542	1.8936	0.0070	1725.64	2352.2
370	210.29877	–13.558	4.1094	4.8098	2.2068	0.0050	1843.33	2235.2
373	217.98862	–13.751	4.2259	4.6537	2.4852	0.0041	1912.45	2153.2

a. Values computed according to the Steam-NBS function implemented in the program EES (Klein et. al, 1991).

Estimate of the temperature dependence of vapor pressure. We can get a first impression of the dependence of the vapor pressure on temperature, if we use the formulas for the temperature dependence of the ideal gas and incompressible fluids from Section 8.4. In other words, we treat the vapor as an ideal gas, and the liquid as incompressible. With Equ.(8.54), the chemical potentials of the two fluids are

$$\begin{aligned} \mu_g &= \mu_g^0 + RT\ln\left(\frac{P_v}{P_0}\right) + \bar{c}_{pg}\left(T - T_0\right) - T\,\bar{c}_{pg}\ln\left(\frac{T}{T_0}\right) - \left(T - T_0\right)\bar{s}_{0g} \\ \mu_l &= \mu_l^0 + \left(P_v - P_0\right)\bar{\upsilon}_{0l} + \bar{c}_{pl}\left(T - T_0\right) - T\,\bar{c}_{pl}\ln\left(\frac{T}{T_0}\right) - \left(T - T_0\right)\bar{s}_{0l} \end{aligned} \qquad (15.15)$$

The pressure term in the chemical potential of the liquid and the terms with the temperature coefficients of enthalpy are relatively small compared to the entropy terms. Accepting this additional approximation, the condition of equilibrium leads to

$$\ln\left(\frac{P_v}{P_0}\right) = -\frac{1}{RT}\left\{\left(\mu_g^0 - \mu_l^0\right) - \left(T - T_0\right)\left(\bar{s}_{0g} - \bar{s}_{0l}\right)\right\} \qquad (15.16)$$

We can use this result to compute the temperature for which the vapor pressure is the standard pressure of 1 atm. The values of Table 6.2 yield a temperature of 97°C, which is acceptably close to the actual value considering the approximations made.

15.1.4 The Clapeyron Equation

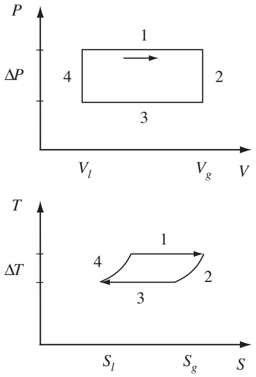

Figure 15.11: A pure simple fluid is allowed to go through a cycle including vaporization and condensation. The energy released in the fall of entropy is equal to the energy exchanged in the mechanical process. The curves are to be found in the bell-shaped area, where a mixture of liquid and vapor exists.

Considering that the vapor pressure is only a function of temperature, its values can be found. All we need to know are a starting value and the change of vapor pressure with temperature. As you will see shortly, the laws of thermodynamics provide for a relation between the derivative of the vapor pressure with respect to temperature and changes of properties of the fluid. The initial value is delivered by a single observation such as the one which tells us that at a temperature of 100°C the vapor pressure of water must be 1 atm.

In Section 10.2.6, a formal derivation of the following result was given. Here, we will consider a cyclic process of a substance which undergoes evaporation and condensation. Take a four step cycle which starts with the evaporation of a fluid at constant temperature and pressure (Fig. 15.11). The change of volume is from V_l to V_g, while the entropy changes from S_l to S_g (both changes are positive). Next, let the gas be cooled just a little bit at constant volume so that the temperature decreases by a very small amount ΔT. At this slightly lower temperature, allow the vapor to condense; this process will again take place at constant pressure. The volume returns to V_l, and very nearly the same amount of entropy is emitted as was absorbed during vaporization. This will be the case if the second step is made so small that it does not add considerably to the overall balances. Finally, the liquid is brought back to the initial state by a slight heating at constant volume.

The cycle described is that of a heat engine. We can evaluate the energy released in the fall of entropy, and the energy used for the mechanical process, and equate them (remember that steps 2 and 4 of the cycle do not contribute much to the balances):

$$\left(\bar{s}_g - \bar{s}_l\right)\Delta T = \left(\bar{\upsilon}_g - \bar{\upsilon}_l\right)\Delta P \qquad (15.17)$$

This is the relation between changes of temperature and changes of vapor pressure we have been looking for; it can be brought into the form known as *Clapeyron's equation*:

$$\frac{dP}{dT} = \frac{\bar{s}_g - \bar{s}_l}{\bar{v}_g - \bar{v}_l} \tag{15.18}$$

If you wish, you can express the change of the entropy from the liquid to the vapor state using the enthalpy of the fluid, Equ.(15.5).

QUESTIONS

1. When water is evaporated, how much of the added entropy and energy will be in the steam?
2. What can be said about the chemical potentials of liquid and vapor (or solid and liquid) along the corresponding pressure-temperature function separating the phases in the *PT* phase diagram of Fig. 15.7?
3. Consider the *TS* diagram of the phase transition from liquid to vapor in Fig. 15.5. At which points or along which lines are the chemical potentials of liquid and vapor equal?
4. If the vapor pressure curve for water is to be calculated on the basis of the models of incompressible fluid and ideal gas, which relations must be used?

EXAMPLE 15.1. Change of melting point of water with a change of pressure.

Determine the change of pressure accompanying a change of the melting point of ice. (a) Calculate the temperature and the pressure coefficients of the chemical potential of water and ice for 0°C, and then use Clapeyron's equation. The temperature coefficients of enthalpy of water and of ice are 4200 J/(K·kg) and 2100 J/(K·kg), respectively. (b) Use the fact that the energy needed to melt ice is 334 kJ/kg. (See also Example 6.5.)

SOLUTION: (a) Modeling water and ice as bodies with constant temperature coefficients of enthalpy, we can calculate their change of entropy from standard temperature to 0°C:

$$\bar{s}\left(T_f\right) = \bar{s}_0 + \bar{c}_P \ln\left(\frac{T_f}{T_0}\right)$$

Considering that the molar entropy is the negative temperature coefficient of the chemical potential given in Table 6.2, we obtain for it:

$$\bar{s}(0°\mathrm{C}) = 44.8 + 0.018 \cdot 2100 \cdot \ln\left(\frac{273}{298}\right) = 41.5\frac{\mathrm{J}}{\mathrm{K \cdot mole}}$$

For liquid water, the figure is 63.3 J/(K · mole). Note that the pressure coefficients of the chemical potential, i.e., the molar volumes, of ice and of water will not change much from their values in Table 6.2. Now, with Equ.(15.9), the result is

$$\frac{\Delta P}{\Delta T} = -\frac{\alpha_{\mu,liquid} - \alpha_{\mu,ice}}{\beta_{\mu,liquid} - \beta_{\mu,ice}} = -\frac{-63.3 - (-41.5)}{(18.1 - 19.7) \cdot 10^{-6}}\frac{\mathrm{Pa}}{\mathrm{K}} = -1.36 \cdot 10^7\frac{\mathrm{Pa}}{\mathrm{K}}$$

(b) Starting with Clapeyron's equation in the form of Equ.(15.10), we see that the right-hand side can be expressed in terms of the energy supplied to ice as it melts. The entropy and the energy necessary for melting are related by Equ.(15.5), which means that Clapeyron's equation can be written as follows:

$$\frac{\Delta P}{\Delta T} = \frac{\bar{s}_l - \bar{s}_s}{\bar{v}_l - \bar{v}_s} = \frac{1}{T_f}\frac{\bar{h}_l - \bar{h}_s}{\bar{v}_l - \bar{v}_s} = \frac{1}{T_f}\frac{\Delta\bar{h}_{fusion}}{\bar{v}_l - \bar{v}_s}$$

With the value of the latent enthalpy of fusion, we obtain – 138 bar/K for $\Delta P/\Delta T$.

EXAMPLE 15.2. Changes of vapor pressure and enthalpy of vaporization.

(a) Express the approximate result for vapor pressure as a function of temperature in terms of the change of the enthalpy of vaporization. Use the temperature of vaporization at 1 atm as a reference. (b) Determine the vapor pressure and the standard chemical potential of mercury vapor at 25°C.

SOLUTION: (a) First, with a pressure of 1 atm and its corresponding temperature of vaporization as the reference point, the standard chemical potentials of vapor and liquid are equal. Using the relation between the entropy and the enthalpy of vaporization leads to

$$\ln\left(\frac{P_v}{P_o}\right) = \frac{1}{R}\left(1 - \frac{T_{bp}}{T}\right)\left(\bar{s}_{bp,g} - \bar{s}_{bp,l}\right) = \frac{1}{R}\left(\frac{1}{T_{bp}} - \frac{1}{T}\right)\Delta\bar{h}_{v,bp}$$

where *bp* stands for *boiling point*. This means that a measurement of the enthalpy of vaporization yields fundamental information about a fluid (as an ideal gas).

(b) We can apply the result just obtained with $T_{bp} = 630$ K, and 57 kJ/mole for the molar enthalpy of vaporization. This leads to

$$\ln\left(\frac{P_v}{P_0}\right) = \frac{1}{8.31}\left(\frac{1}{630} - \frac{1}{298}\right)57000 = -12.1$$

or $P_v = 0.54$ Pa. This value, in turn, can be used to calculate the chemical potential of gaseous mercury at 25°C and 1 atm. We use the same derivation which led to Equ.(15.14):

$$\ln\left(\frac{P_v}{P_0}\right) = -\frac{1}{8.31 \cdot 298}\left(\mu_g^0 - 0\right)$$

Remember that the standard value of the chemical potential of liquid mercury is set equal to zero. This gives a value of + 30.0 kG (compared to the more accurate figure of 31.84 kG).

EXAMPLE 15.3. The Clausius-Clapeyron equation for the ideal gas.

Derive the expression of the Clapeyron equation as it holds for the ideal gas and show that this is equivalent to the approximation of the pressure-temperature relation for vapor pressure derived in Equ.(15.16) or above in Example 15.2. Assume the enthalpy of vaporization to be constant.

SOLUTION: Written using the enthalpy of vaporization, Clapeyron's equation becomes

$$\frac{dP}{dT} = \frac{\bar{s}_g - \bar{s}_l}{\bar{v}_g - \bar{v}_l} = \frac{1}{T}\frac{\bar{h}_g - \bar{h}_l}{\bar{v}_g - \bar{v}_l} = \frac{1}{T}\frac{\Delta\bar{h}_v}{\bar{v}_g - \bar{v}_l}$$

For the ideal gas, we use the equation of state, and we neglect the volume of the liquid phase compared to its value in the vapor phase. Therefore, the equation becomes

$$\frac{dP}{dT} = \frac{1}{T}\frac{\Delta\bar{h}_v}{\bar{v}_g} = \frac{1}{T}\frac{\Delta\bar{h}_v}{RT/P} = \frac{P}{RT^2}\Delta\bar{h}_v$$

Integration of this equation yields

$$\ln\left(\frac{P}{P_0}\right) = \frac{1}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\Delta\bar{h}_v$$

which is equivalent to what was derived before. Clapeyron's equation specialized to the ideal gas is called the Clausius-Clapeyron equation.

15.2 MIXTURES OF TWO-PHASE FLUIDS: MOIST AIR

In this section, we will discuss one more application of the ideas of chemical transformation, namely the thermodynamics of mixtures of two ideal gases when one can undergo phase changes. Moist air furnishes such an example—dry air and water vapor. While the air itself is a mixture, it can be treated as a single component, since in the range of temperature and pressure found in our atmosphere, its constituents all behave identically as ideal gases; in other words, we do not notice that dry air itself is composed of different parts. The case of the second component, however, is quite different. With liquid (or solid) water present, water vapor in the air can condense (or directly turn into frost or ice); or water can evaporate (and ice can sublimate). Thus, the conditions in the atmosphere are such that water can undergo phase transitions. We are all familiar with water condensing on window panes on a cold day, droplets forming on a pipe carrying cold water, dew accumulating on the grass in the morning, or frost forming on the ground.

These and their reverse processes can again be understood as chemical phenomena. When vapor condenses out of moist air, this simply means that, under the given circumstances, the chemical potential of the water vapor is larger than that of the liquid phase. On the other hand, when water evaporates from the surface of a pond, the tendency of liquid to go into the vapor phase is stronger than the reverse drive.

We can use our knowledge of the concepts of vapor pressure and chemical equilibrium between phases to state these observations in more precise language. Consider evaporation of water into the air above a liquid surface (as in Fig. 15.12). Obviously, if water diffuses from the liquid into the air, chemical equilibrium has not been attained. There is less water vapor in the air than there could be under the condition of equilibrium, or, put differently, the gas above the water surface is said to have a humidity which is smaller than the humidity at saturation. When the air is saturated with water vapor, the chemical potential of the vapor phase and of the liquid phase are equal, and there are equal rates of water evaporating and vapor condensing.

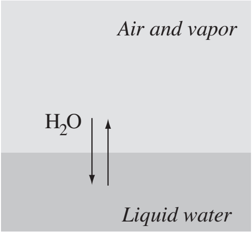

Figure 15.12: If a mixture of dry air and water vapor is present together with liquid water, the vapor component of the gas can undergo phase transitions. At chemical equilibrium, the air is said to be saturated with water vapor.

To give you an impression of the amount of water vapor present in the air, consider standard conditions of temperature and pressure. You know that at 25°C, the vapor pressure of water is about 3000 Pa or 0.030 bar (see Table 15.1). As we have seen before, it hardly matters that the pressure of the liquid is 1 atm because of the presence of the air: the chemical potential of liquid water changes only slightly when its pressure changes. Therefore, the value of the vapor pressure calculated under the assumption that only water is present can be used perfectly well in the present case. We can now say that at saturation the amount of water in the air is 0.03 mole per 1 mole of air (equivalent to about 20 g of H_2O in 1 m^3 of air). With such numbers, it is clear that the vapor component also behaves as an ideal gas. As far as the body of moist air is concerned, we can treat it as a mixture of two ideal gases and apply the rules found in Section 6.6.3.

15.2.1 Description of the State of Moist Air

It is customary to define two interrelated quantities with whose help the state of moist air can be described. These are the *humidity ratio* (also called specific humidity or absolute humidity), and the *relative humidity*. First, it should be clear that the pressure of the mixture is P, while the partial pressures of dry air and of vapor are P_a and P_v, respectively, with

$$P = P_a + P_v \tag{15.19}$$

The humidity ratio ω is defined as the ratio of the mass of water vapor m_v and the mass of dry air m_a:[1]

$$\omega \equiv m_v / m_a \tag{15.20}$$

Using the equation of state of the ideal gas this can be transformed into

$$\omega = \frac{M_{0v} P_v}{M_{0a} P_a} = 0.622 \frac{P_v}{P - P_v} \tag{15.21}$$

The numerical value 0.622 applies for dry air and water. The second quantity introduced, the relative humidity ϕ, is defined as the ratio of the amount of water vapor actually present and the amount present when the air is saturated with vapor:

$$\phi \equiv n_v / n_{v,sat} \tag{15.22}$$

The laws of ideal gases let us change this to

$$\phi = \frac{y_v}{y_{v,sat}} = \frac{P_v}{P_g} \tag{15.23}$$

where P_g is the saturation vapor pressure at the temperature under consideration (in the following, the index g will be used to indicate saturation). Note that the relative humidity and the humidity ratio are convenient definitions for expressing the case of moist air in terms of the laws of mixtures of ideal gases introduced in Section 6.6.3. As far as physics is concerned, nothing new has been formulated. What we can say, however, is that at a relative humidity smaller than 1, the chemical potential of the vapor μ_v is smaller than its value for the condition at saturation μ_g, the change stemming from the difference in actual vapor pressure from the saturation pressure. Therefore

$$\mu_v = \mu_g + RT \ln \phi \tag{15.24}$$

Since the temperature is the same for the actual condition and for the assumed condition of saturation, the enthalpy of the vapor is what it would be at saturation:

---

[1] Sometimes, the specific humidity is defined as the ratio of mass of water vapor m_v to mass of (humid) air m:

$$\omega \equiv m_v / m$$

and therefore differs slightly from the humidity ratio.

$$h_v = h_g \tag{15.25}$$

This holds for an ideal gas (see Fig. 15.29 for actual values). Therefore, the entropy of the vapor (s_v), deviates from its value at saturation (s_g):

$$\bar{s}_v = \bar{s}_g - R\ln\phi \tag{15.26}$$

15.2.2 The Dew Point

Assume a state of moist air with a relative humidity less than the saturation value of 1. This means that the chemical potential of the vapor at the given temperature is smaller than the potential of the liquid phase (Fig. 15.13). Now, what happens if the temperature of the mixture and the liquid water decreases? The chemical potentials of the vapor and the liquid phase increase, but not at the same rate. From Table 6.2, we see that the magnitude of the slope for the gaseous phase is greater, which means that the potentials become equal at a particular value of the temperature. At this point, water vapor in the air will begin to condense. For obvious reasons, this temperature is called the *dew point*. Using a table of saturation vapor pressure, dew points can be easily computed (Example 15.4). Here, we will give a formal derivation assuming the validity of the ideal gas model.

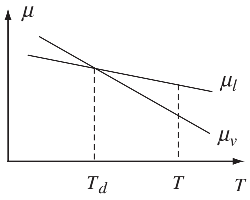

Figure 15.13: At a value of the relative humidity which is less than 1, the chemical potential of the vapor is smaller than that of liquid water. Decreasing the temperature leads to a condition for which the potentials are equal: condensation of water vapor sets in.

We have to find the temperature for which the chemical potentials of the vapor in the air and of the liquid water phase are equal, given a starting condition at temperature T_0 and pressure P_0. The chemical potential of the liquid changes from the standard value only because of the change of temperature:

$$\mu_l(T_d) = \mu_l^0 - (T_d - T_0)\bar{s}_{0l} \tag{15.27}$$

The potential of the vapor, on the other hand, is different from the standard value for two reasons: the pressure P_v at temperature T_0 is different from P_0; and the temperature is now at the dew point:

$$\mu_v(T_d) = \mu_g^0 + RT_d \ln\left(\frac{P_v}{P_0}\right) - (T_d - T_0)\bar{s}_{0g} \tag{15.28}$$

Now, the actual vapor pressure P_v can be expressed in terms of the saturation value if we introduce the relative humidity:

$$\begin{aligned} \mu_v(T_d) &= \mu_g^0 + RT_d \ln\left(\frac{\phi P_{g0}}{P_0}\right) - (T_d - T_0)\bar{s}_{0g} \\ &= \mu_g^0 + RT_d \ln\left(\frac{P_{g0}}{P_0}\right) + RT_d \ln\phi - (T_d - T_0)\bar{s}_{0g} \end{aligned} \tag{15.29}$$

Equating the chemical potentials, i.e., Equations (15.27) and (15.29), furnishes a nonlinear condition for the unknown temperature of the dew point. We need only the saturation pressure P_{g0} at the original temperature T_0, which can be calculated from the approximation given in Equ.(15.16) or found in tables. The formulas are rather accurate, and compare well with the measured values found in steam tables. Remember that, apart from the assumption of validity of the ideal gas model, we have neglected some terms in the temperature dependence of the chemical potentials.

15.2.3 Adiabatic Saturation and Wet Bulb Temperature

Below, an equation will be used that relates the humidity ratio of moist air to the wet bulb temperature. The process taking place around a wet bulb thermometer is similar to the model of adiabatic saturation that will be discussed now.

Adiabatic saturation. Take a stream of moist air passing over the surface of some water as in Fig. 15.14. The air picks up extra moisture until it is saturated. Since no conductive transfer of entropy is involved, the process is called *adiabatic saturation*. Consider a control volume encompassing a section of the air stream and a small part of the water which delivers the moisture. In a steady state, the amount of water vapor flowing out with the saturated air will be the sum of the mass entering with the somewhat dryer air, and the mass of the water evaporating from the surface (this latter mass is replenished through the control surface):

$$\left|I_{m,a}\right| + \left|I_{m,v1}\right| + \left|I_{m,l}\right| = \left|I_{m,a}\right| + \left|I_{m,v2}\right| \tag{15.30}$$

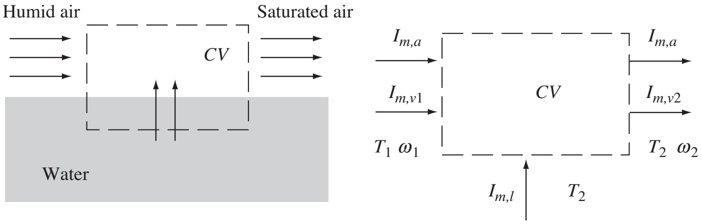

Figure 15.14: A stream of moist air passes over a water surface and picks up additional water until it is saturated. The air cools to T_2, and in the steady state, the water will have the same temperature (if the body of water is not too large).

Here, a, l, and v denote dry air, liquid water, and water vapor, respectively. For the balance of energy, we will assume the velocity terms to be negligible. Also, the moist air will be considered to be a simple mixture of dry air and water vapor at total pressure P. At the inlet, the temperature is T_1, and the humidity ratio is ω_1, while at the outlet we have T_2 and ω_2 (in the saturation process, the incoming air is assumed to cool to the temperature of the water which is at T_2). Now, the energy currents can be written in terms of the enthalpy of the fluids (see Equ.(8.40)):

$$h_a(T_1)\left|I_{m,a}\right| + h_v(T_1)\left|I_{m,v1}\right| + h_l(T_2)\left|I_{m,l}\right| = h_a(T_2)\left|I_{m,a}\right| + h_g(T_2)\left|I_{m,v2}\right| \tag{15.31}$$

As before, the index g is used for the saturated vapor state. Using the balance of mass we can express the current of water from the reservoir. Dividing by the current of mass of dry air introduces the humidity ratio. If we also replace the enthalpy of the unsaturated vapor at T_1 by the corresponding value for the saturated state at T_2 (remember Equ.(15.25)), we get:

$$h_a(T_1) + \omega_1 h_g(T_1) + (\omega_2 - \omega_1)h_l(T_2) = h_a(T_2) + \omega_2 h_g(T_2) \tag{15.32}$$

Wet bulb temperature. The condition of an ideal gas of constant amount of substance is fixed by two values such as the pressure and the temperature. A third value is obviously needed if a mixture such as moist air is described for which the amount of vapor can change. A suitable third value might be the humidity ratio. However, humidity is not so readily measured, which is why it would be simpler to specify an additional temperature. Here, we will show how the temperature measured by a thermometer whose bulb is surrounded by a wet wick can be used to find the humidity of the air.

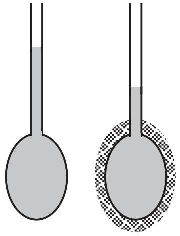

Figure 15.15: Dry and wet bulb thermometers for measuring the humidity of air. A wick saturated with water surrounds the second thermometer. If the air is not saturated, this thermometer will show a lower temperature than the dry bulb instrument.

The temperature measured by a simple thermometer is called the dry bulb temperature of the moist air. If you surround the bulb of the thermometer with a wick saturated with water, it will show a lower temperature for the same conditions of the air, the value being called the wet bulb temperature (Fig. 15.15). The reason for the lower temperature is this: As the air, which is assumed to be not saturated, passes over the bulb with the wick, water will evaporate, increasing the humidity of the air. Indeed, we will assume the air to become saturated by the process—analogous to the process of adiabatic saturation discussed above, meaning that the saturated air has the same temperature as the water. The entropy necessary to vaporize the water in the wick comes from the water and from the air itself, which means that the temperature of the stream of air leaving the wick is lower than the normal air temperature. This new temperature is the temperature taken by the water in the wick; therefore, the wet bulb thermometer shows the lower temperature of the saturated air.

If the wet bulb thermometer is ventilated properly, the process taking place here is a close approximation to *adiabatic saturation*. It is specified by the temperatures and humidities of the original moist air and of the saturated air. The value of the humidity ratio can then be calculated from Equ.(15.32):

$$\omega = \frac{h_a(T_{wb}) - h_a(T) + \omega'\left[h_g(T_{wb}) - h_l(T_{wb})\right]}{h_g(T) - h_l(T_{wb})} \qquad \textbf{(15.33)}$$

where ω' is computed according to Equ.(15.21) for the saturated air at the wet bulb temperature, i.e.,

$$\omega' = 0.622\frac{P_g(T_{wb})}{P - P_g(T_{wb})} \qquad \textbf{(15.34)}$$

The condition of adiabatic saturation may be satisfied by the wet bulb thermometer only to a limited extent. The real wet bulb phenomenon is influenced by the rate of evaporation and the rate of diffusion through the wick. Still, the agreement is acceptable, and the wet bulb temperature is commonly used as the representation of the adiabatic saturation temperature.

QUESTIONS

5. In general, is the molar entropy of water vapor in the air smaller than, equal to, or larger than at saturation? Why is this so?
6. Why is moist air less dense than dry air (at the same temperature and pressure)? What does this mean for moist air coming off vegetation, the ground, or lakes?
7. Why can we assume that the enthalpy of water vapor in moist air is generally equal to the enthalpy of the vapor if the air is saturated with moisture?
8. In practice, what is the condition for the stream of air exiting the adiabatic saturator in Fig. 15.14 to be saturated and have the same temperature as the water (T_2)?

EXAMPLE 15.4. Calculating a dew point using tabular data.

(a) At a temperature of 30°C and standard pressure, the relative humidity of air is measured at 75%. Determine the temperature at which water vapor would begin to condense. Use the data given in Table 15.1. (b) The temperature of the air drops to 20°C. What fraction of the vapor present in the air will condense?

SOLUTION: (a) At 30°C, the saturation vapor pressure is 4246 Pa. With a relative humidity of 75%, the actual vapor pressure (the partial pressure of the water vapor in the air) is

$$P_v = \phi P_g = 0.75 \cdot 4246\,\text{Pa} = 3185\,\text{Pa}$$

The value of 3185 Pa almost precisely corresponds to the saturation vapor pressure at 25°C. This means that at 25°C, the air would be saturated with the amount of water vapor it actually contains, and the vapor would begin to condense.

(b) At 25°C and with a vapor pressure of 3185 Pa, the air could just retain the initial amount of water present at a relative humidity of 100%. At 20°C, however, the vapor pressure is only 2340 Pa. If we allow for 100% relative humidity at that state, the air could contain only the fraction 2340/3190 = 0.73 of the initial amount of water. An initial amount of

$$n_{vo}/V = \frac{P}{RT} = \frac{3184}{8.314 \cdot 298}\frac{\text{mole}}{\text{m}^3} = 1.29\frac{\text{mole}}{\text{m}^3}$$

will be reduced to 0.94 mole/m^3. For every cubic meter of air, 6.3 g of water will condense.

EXAMPLE 15.5. The height above ground of cloud formation

Make the following model of the vertical circulation of air. Moist air (not saturated) rises adiabatically due to convective instability. With a relative humidity of 0.50, and standard pressure and temperature at the ground, calculate the level above ground at which condensation of the water vapor should set in. Explain why this happens for a temperature which is lower than the dew point calculated for the ground.

SOLUTION: The quantities which are constant for the process are the entropy and the humidity ratio. (Before the onset of condensation, the amount of water vapor in the air remains constant.) One therefore should calculate these two quantities for the conditions at the ground. In functional form, this might look like

```
so = Entropy(AirH2O,T=298,P=100,R=0.5)
w = HumRat(AirH2O,T=298,P=100,R=0.5)
```

Tables (or computer programs) yield values of 5.788 kJ/(K · kg) and 0.00992, respectively. After this preparation, values of the temperature, and the specific volume can be taken from tables as a function of decreasing pressure. Again, using functions implemented in EES (Klein et al., 1991), we have

```
so = Entropy(AirH2O,T=T,P=P,w=w)
v = Volume(AirH2O,T=T,P=P,w=w)
```

Then, using the law of hydrostatic equilibrium, the volume can be integrated over the pressure to yield the height as a function of pressure:

$$dh/dP = -1/g\rho = -\upsilon/g$$

Finally, the chemical potential of liquid water and of water vapor have to be expressed:

```
mu_l = Mo*(Enthalpy(Water,T=T,X=0)–T*Entropy(Water, T=T,X=0))
```

```
mu_v = Mo*(Enthalpy(Water,T=T,P=Pv)–T*Entropy(Water, T=TP=Pv))
w = 0.622*Pv/(P–Pv)
```

Results are given in Table 15.2 and in the accompanying graph (Fig. Ex.5.1). The graph shows that, up to a certain height (about 1400 m, temperature of 284.5 K), the chemical potential of the vapor is smaller than that of liquid water (the chemical potential of liquid water increases because of the effect of decreasing temperature). At this point, the relative humidity becomes 1. We therefore expect cloud formation to begin at about this level above ground.

Table 15.2: Properties of moist air at constant entropy and humidity ratio

P / kPa	T / K	υ / m^3/kg	h / m	μ_l / kG	μ_v / kG
100	298.0	0.869	0	–0.0838	–1.7880
98	296.3	0.882	178	–0.0729	–1.5647
96	294.6	0.895	360	–0.0625	–1.3383
94	292.8	0.909	543	–0.0527	–1.1085
92	291.0	0.923	730	–0.0436	–0.8752
90	289.2	0.937	920	–0.0350	–0.6382
88	287.4	0.952	1110	–0.0271	–0.3976
86	285.5	0.968	1310	–0.0200	–0.1530
84	283.6	0.985	1510	–0.0135	–0.0135

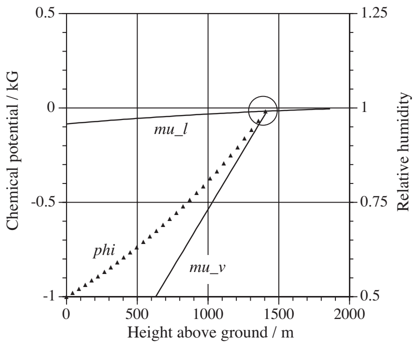

Figure Ex.5.1

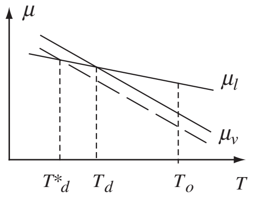

Figure Ex.5.2

The dew point calculated for the values at the ground, on the other hand, is 286.9 K. A plot of the chemical potential of liquid water and water vapor as a function of temperature can demonstrate the influence of a change of pressure upon the dew point. Lowering the pressure leaves the potential of the liquid more or less unchanged, while that of the vapor decreases. This shifts the line representing the chemical potential of the vapor downward, leading to an intersection with the line for the liquid at a lower temperature.

EXAMPLE 15.6. Calculating the wet bulb temperature of moist air.

Take the same conditions for moist air as in Example 15.4 (75% relative humidity at 30°C and 1 atm). How large is the corresponding wet bulb temperature?

SOLUTION: In addition to the definition of relative humidity in terms of the vapor pressure and the saturation vapor pressure, we will need to simultaneously solve Equ.(15.21), Equ.(15.33) and Equ.(15.34). For the stated problem, namely finding the wet bulb temperature, the equations are nonlinear. We will have to find the values of enthalpies and pressures for the quantities appearing in the equations, partly for the still unknown value T_{wb}. Below you will find the relations to be set up if the thermodynamic property data are given in the form of programmed functions. Compare the solution of these equations with a solution attempted using tabulated values.

```
Given data:   phi = 0.75
              T1 = 30
              P1 = 101.3
Properties:   ha_T = Enthalpy(Air,T=T1)
              ha_Twb = Enthalpy(Air,T=Twb')
              hg_T = Enthalpy(Steam,T=T1,X=1),
              hg_Twb = Enthalpy(Steam,T=Twb,X=1)
              hl_Twb = Enthalpy(Steam,T=Twb,X=0)
              Pg_Twb = Pressure(Steam,T=Twb,X=1)
              Pg_T = Pressure(Steam,T=T1,X=1)
Relations:    w = ((ha_Twb–ha_T)+w'*(hg_Twb–hl_Twb))/(hg_T–hl_Twb)
              w' = 0.622*Pg_Twb/(P1–Pg_Twb)
              w = 0.622*Pv_T/(P1–Pv_T)
              phi = Pv_T/Pg_T
Solution:     ha_T = 303.6 kJ/kg        ha_Twb = 299.9
              hg_T = 2555               hg_Twb = 2549
              hl_Twb = 110.2
              P1 = 101.3 kPa            Pg_T = 4.246
              Pg_Twb = 3.425            Pv_T = 3.184
              phi = 0.750
              T1 = 30.0°C               Twb = 26.3
              w = 0.0202                w' = 0.0218
```

The solution of the problem was performed completely within the program EES (Klein et al., 1991). The form of the property functions is pretty much self explanatory. *Air* stands for dry air, while *Steam* denotes water (liquid and vapor). The temperature and its wet bulb counterpart are denoted by T and Twb, respectively, while w is used for the humidity ratio. X is the quality (defined in Equ.(15.59); X=0 is for saturated liquid, while X=1 is for saturated vapor).

15.3 EVAPORATION

The term evaporation is most commonly used to describe vaporization of some water from a larger body of water and subsequent transfer of the vapor into the air surrounding the body of water. In this section, evaporation or condensation of water, and the mixing of water vapor with air will be considered from a dynamical perspective. Such processes are important in nature (think of the evaporation of water from lakes, from soil, or from leaves), in chemical engineering (where we let other substances evaporate as well), in power engineering (cooling towers), and in air conditioning.

15.3.1 Evaporation and Diffusion of Water Vapor in Air

Consider a body of water with unmoving air above it. If the air is not saturated, there is a difference of chemical potentials between the liquid water and the water vapor in the air leading to the transfer of more water vapor into the air. Water must evaporate, so the concentration of vapor will be higher in a layer adjacent to the body of water than further away from it. As a result, the vapor diffuses upward into the drier air (see Fig. 15.16).

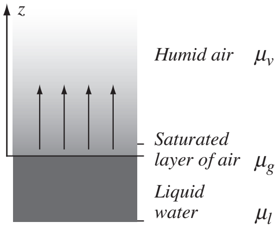

Figure 15.16: Evaporation from a body of water can be understood as the diffusion of water vapor from a saturated layer of air near at the surface of the water to points further away where the air is not saturated.

This process continues until the air above the water is saturated. If it is continuously removed—which normally is the case in an open space—evaporation from the surface of the body of water continues as long as liquid water remains. Evaporation does not depend upon the water being warmer than the air. In fact, the process described works even when the water is cooler than the air. All that is needed is a higher concentration of water vapor near the surface of the water compared to points further away.

Evaporation of warm water: a simple model. Hot water is poured into a glass and placed on a scale. The water stands at a depth d from the top of the container (see Fig. 15.17, left). Mass, water and air temperature, and relative humidity are measured as functions time. The temperature decreases as a result of cooling (Fig. 15.17, right) which is mostly due to evaporation: the mass of the water decreases quite steeply at higher temperatures whereas the flow of vapor into the air decreases to a lower and almost constant value for water temperatures close to the temperature of the air (see Fig. 15.17, center).

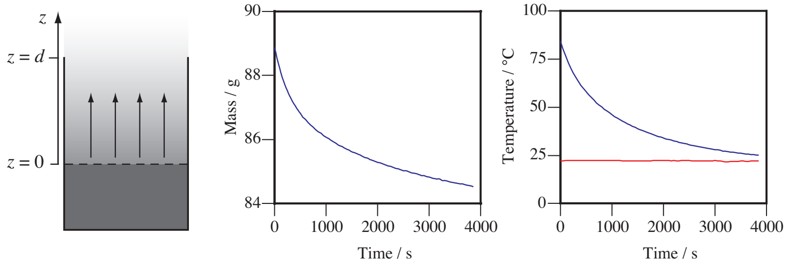

Figure 15.17: Evaporation of water in a glass open at the top (left). Mass (center) and water and air temperature (right) have been measured as functions of time. The relative humidity during the experiment was 0.20.

If evaporation is due to the diffusion of vapor from the surface of the liquid at $z = 0$ a distance d through the air, we can formulate a simple relation for the flow of amount of substance of water vapor (remember Section 6.7):

$$I_{n,v} = -Ah_v\left(\bar{c}_d - \bar{c}_0\right) \qquad \textbf{(15.35)}$$

Here, $\bar{c}$ stands for the concentration of vapor in the air at $z = d$ and $z = 0$, respectively. h_v is transfer coefficient for amount of substance, and A symbolizes the cross section of the water surface. If we treat the vapor as an ideal gas, its concentration is proportional to its partial pressure. Therefore, Equ.(15.35) transforms into

$$I_{n,v} = -\frac{Ah_v}{RT_a}\left(\phi P_g\left(T_a\right) - P_g\left(T_w\right)\right) \qquad \textbf{(15.36)}$$

P_g is the saturation vapor pressure and ϕ denotes the relative humidity. Here, I have assumed that the vapor is always at the temperature of the air, T_a, even near the surface of the water which is at T_w. In the layer at the surface of the body of water, the air is saturated. The transfer coefficient h_v will depend upon the depth of the water in the container, and upon the diffusivity of water vapor in air.

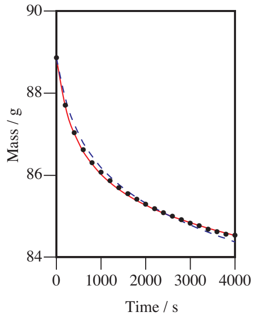

Figure 15.18: Evaporation of hot water from an open container as in Fig. 15.17. Dots are measured values of the mass of the remaining water. The dashed line is the result of the model presented in Equ.(15.36). The solid line results from a version of the model in Equ.(15.44).

If the measured temperatures (Fig. 15.17) are used to predict the flow of mass $I_{m,v} = M_{0v} I_{m,v}$ from the surface of the water, we get the dashed line shown in Fig. 15.18; at first sight, it compares relatively well with the measured mass (dots) but clearly shows different behavior. For this reason. let us extend the model to one which includes the spatial variation of conditions in the container of Fig. 15.17.

Diffusion of vapor in air. First, we have to understand the precise nature of the transports in the container of Fig. 15.17 in the column of moist air above the body of water. Let us assume that there is variability in the vertical direction only, and that the situation is in steady-state. There must certainly be a conductive (diffusive) flux of water vapor whose current density of amount of substance at a point z in the column of humid air will be abbreviated by j_{nv} (Fig. 15.19). In a mixture of gases such as dry air and water vapor, if one of the components diffuses in one direction, there must be an equal diffusive flux of the other component in the opposite direction. This is so because, in steady-state, one mole (or one molecule) of vapor must be replaced by one mole (or one molecule) of air. So we have a current density of dry air j_{na} at point z.

The downward flux of air has important consequences. If there were nothing to balance it, air would accumulate at the surface of the water. Since this is not the case, we need a convective (or bulk) flux of humid air going up where the flux of (dry) air must equal the diffusive downward flux of (dry) air. Since the air is humid, water vapor is transported convectively, so we have an additional flux of water vapor going upward (see Fig. 15.19).

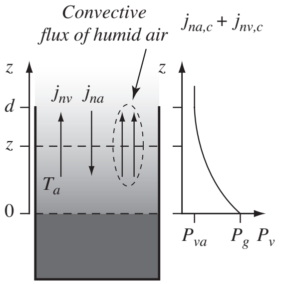

Figure 15.19: Evaporation of water in a container as in Fig. 15.17. There are several different currents of vapor and air (left). The diagram on the right shows the form of the vapor pressure in the column of air.

The laws of balance of amounts of substance (of air and of water vapor) and coupling between the fluxes can be formulated quite simply. First, we should note that the fluxes are independent of position z since we have steady-state conditions. Second, the diffusive flux density of air is equal in magnitude to the diffusive flux density of water vapor:

$$j_{nv}(z) = -j_{na}(z) \tag{15.37}$$

Since air has to remain balanced in the column above the body of water, we have

$$j_{na,c}(z) = -j_{na}(z) \tag{15.38}$$

The subscript c stands for convective transports. Finally, there is the convective transport of vapor which is coupled to the convective flux of air. Since the amount of vapor in the air equals the molar fraction of the amount of humid air, we have

$$j_{nv,c}(z) = \bar{x}_v \left(j_{na,c}(z) + j_{nv,c}(z) \right) \tag{15.39}$$

(The current of humid air equals the sum of currents of air and vapor.) Now, the total current density of vapor is the sum of its diffusive and convective parts which leads to:

$$j_{nv,tot}(z) = \frac{1}{1 - \bar{x}_v} j_{nv}(z) \tag{15.40}$$

Now, constitutive relations have to be introduced. For one, the diffusive current density of vapor can be formulated as in Section 6.7.2:

$$j_{nv}(z) = -D\frac{\partial \bar{c}_v}{\partial z} \tag{15.41}$$

(The diffusivity of water vapor in air is about $2.4 \cdot 10^{-5}$ m²/s at 300 K.) Furthermore, the concentration of water vapor can be expressed in terms of the pressure of this component by using the ideal gas relation:

$$\bar{c}_v(z) = \frac{1}{RT_a}P_v(z) \tag{15.42}$$

For isothermal situations, the temperature is equal to the ambient temperature everywhere. If we introduce Equations (15.41) and (15.42) into Equ.(15.40) and integrate the first order differential equation from $z = 0$ to $z = d$, and remember that the current densities are constant, we obtain

$$I_{nv} = D\frac{P}{RT_a}\frac{A}{d}\ln\left(\frac{P - P_{va}}{P - P_g}\right) \tag{15.43}$$

A denotes the cross section of the container from which water evaporates, and P_{va} and P_g are the water vapor pressure in the air far from the container (given by its temperature and relative humidity) and the saturation vapor pressure at the same temperature, respectively.

Evaporation of hot water. Let us revisit the experiment described in Fig. 15.17. The water is hotter than the environment for most of the time, so we do not have isothermal conditions as assumed in the derivation performed above. If we assume the column of air above the water to be at T_a, and the water at T_w, we could apply Equ.(15.43) and get a simple result:

$$I_{nv} = D\frac{P}{RT_a}\frac{A}{d}\ln\left(\frac{P - P_{va}(T_a)}{P - P_g(T_w)}\right) \tag{15.44}$$

Interestingly, the pressure dependence of this expression fits data well, as shown by the solid line and the dots in Fig. 15.18. However, for an actual fit, the current in Equ.(15.44) has to be multiplied by a constant factor of the order of 10. While the form of Equ.(15.44) seems to apply to the evaporation of hot water from a container, the strength of the current is considerably larger than predicted by the simple model. Furthermore, experiments with different values of the depth of the water level do not show the dependence on d expected from Equ.(15.43) or (15.44). Vapor condenses on the inside of the glass container and evaporates again at different heights and joins the vapor coming from the surface of the body of water. This may explain the differences.

15.3.2 Evaporative Cooling

Evaporative cooling can be taken to mean two different things. On the one hand, bodies (solids, liquids) are cooled if a liquid at their surfaces evaporates. We have seen this effect several times already such as in the drop of temperature of a wet thermometer (Fig. 6.8). On the other hand, we may direct our attention to the air that is involved in evaporation and takes up vapor; its temperature is reduced. This plays a role in air-conditioning: in a hot and dry climate, we may want the comfort of cooler and more humid air. Below, two applications will be discussed: forcing dry air through a wet pad and the cooling of already cold water sitting in a container.

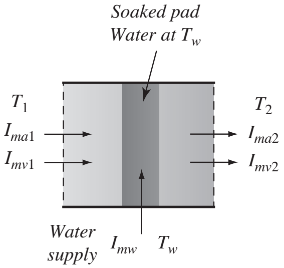

Figure 15.20: Relatively dry, hot air flows through a pad soaked with water. Because of evaporation, the temperature of the humid air exiting the duct is lowered, and its humidity is increased.

Dry air flowing through a wet pad. Consider a simple duct through which air can flow. The temperature of the air is to be lowered by evaporation of water in a pad through which the air is forced (Fig. 15.20). If we assume the system to be thermally insulated and if we can neglect mechanical and gravitational effects, the situation is similar to the one discussed in adiabatic saturation (Section 15.2.3) or to the case of mixing of streams of fluids (Section 8.6.4). For this reason, only the laws of balance will be formulated here.

There are three inflows and two outflows (Fig. 15.20). The steady-state balances of mass for air and water take the form

$$\begin{aligned} I_{ma1} &= I_{ma2} \\ I_{mv1} + I_{mw} &= I_{mv2} \end{aligned} \tag{15.45}$$

The law of balance of entropy contains six terms: one each for the incoming and outgoing substances and the production rate:

$$s_{a1}I_{ma1} + s_{v1}I_{mv1} + s_w I_{mw} + \Pi_S = s_{a2}I_{ma2} + s_{v2}I_{mv2} \tag{15.46}$$

The law of balance of energy only involves the convective currents of energy for the five currents in Fig. 15.20:

$$h_{a1}I_{ma1} + h_{v1}I_{mv1} + h_w I_{mw} = h_{a2}I_{ma2} + h_{v2}I_{mv2} \tag{15.47}$$

At both he inlet and the outlet, the currents of mass of vapor and air are related by the humidity ratios defined in Equ.(15.20). To complete a model, we need expressions for the entropies and enthalpies of air and water or steam for the conditions of temperature, pressure, and humidities that apply in the situation depicted in Fig. 15.20.

Evaporation of cold water. Water having the same temperature as the environment can still become colder by evaporation if it is inside a well insulated container that is open at the top. Historically, in dry climates, water was kept cool by storing it in amphoras which were sprayed with water, and fans were used to keep the air flowing over the wet containers.

Here is an experiment and dynamical model that shows how to deal with this situation. Water having roughly the temperature of the environment is poured into a relatively well insulated container that is open at the top. It is placed on an automatic scale, and water and air temperature, and relative humidity of the environment, are measured as functions of time (Fig. 15.21). We need to track the entropy and mass of the water and the entropy of the container in our model (it turns out that the dynamics of the container has to be taken into account if we want to get a good fit between model and data; see Fig. 15.21, center):

$$\begin{aligned} \dot{S}_w &= -I_{S,evap} - I_{S,cond} \\ \dot{m}_w &= -I_{m,evap} \end{aligned} \tag{15.48}$$

$$\dot{S}_c = -I_{S,ca} + I_{S,cond} \tag{15.49}$$

Note that, in principle, there should be a conductive entropy current going directly from the water to the air (or vice-versa); however, the simulation is not affected greatly by this addition.

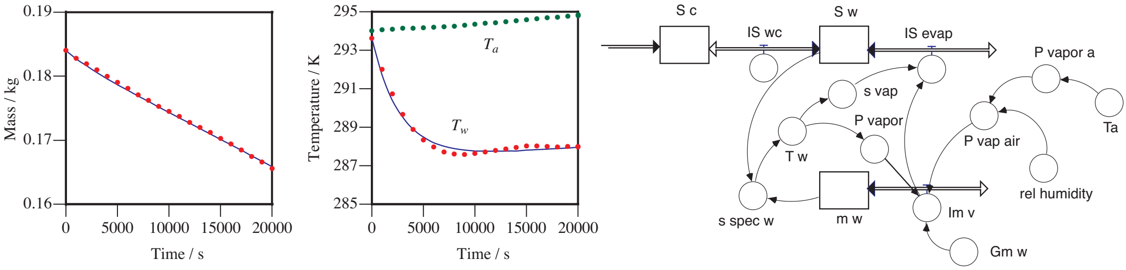

Figure 15.21: Evaporation of cold water in a relatively well insulated container that is open at the top. Mass (left) and water and air temperature (center) have been measured as functions of time (dots denote data). The relative humidity during the experiment was 0.15. Right: Diagram of a system dynamics model. Note that there is more to the model not shown here (top left of the diagram). Here, w, v, a, and c denote water, vapor, air, and container, respectively.

Constitutive laws have been assumed to be as follows. Since temperature differences are fairly small, entropy production due to conductive transfer has been neglected and transport models have been assumed to be linear. In particular, the flow of water evaporating from the surface of the water in the tank is modeled as in Equ.(15.36):

$$I_{m,v} = -G_{m,v}\left(\phi P_g\left(T_a\right) - P_g\left(T_w\right)\right) \tag{15.50}$$

The relation has been formulated for the flux of mass rather than for amount of substance. $G_{m,v}$ is a conductance for mass transfer. Conductive currents of entropy have been written accordingly. Note that the temperature of the water in the tank can be calculated on the basis of its specific entropy which equals the ratio of instantaneous values of entropy and mass. Together with expressions for vapor pressure and the specific entropy of vapor, the missing quantities can be calculated. Here is the relation for the evaporative current of entropy:

$$I_{S,evap} = s_{vap} I_{m,v} \tag{15.51}$$

where s_{vap} is the specific entropy of the steam leaving the surface of the body of water. The model performs quite well (see the solid lines in the diagrams on the left and at the center of Fig. 15.21).

15.3.3 Cooling Towers

Consider cooling towers as a last application of evaporative cooling. Where the cooling needed for a large thermal power plant cannot be done by transferring the entropy to a river, a cooling tower may be used. Here, water used for the condenser of the plant is sprayed into a stream of relatively dry air so that a part of the water evaporates. The portion of the cooling water that does not evaporate has given up entropy. Together with makeup water (used to replenish the flow of water through the condenser), the colder cooling water is returned to the condenser of the plant.

The processes going on can be envisioned in a schematic similar to the one showing evaporative cooling in Fig. 15.20. In place of the wet pad, we have cooling water falling through the stream of air forced through the device. (Naturally, the geometry of an actual cooling tower will be different from what we discuss here, but the processes can still be understood by the schematic shown in Fig. 15.22.)

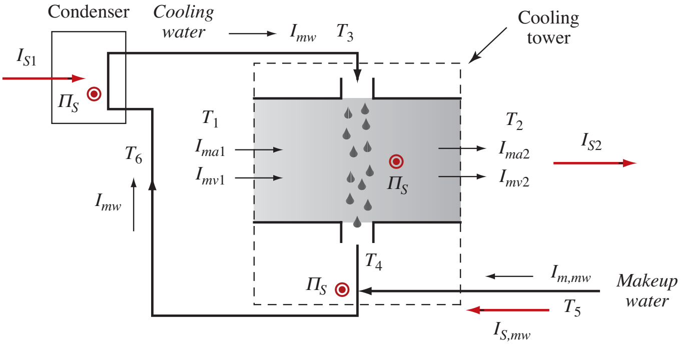

Figure 15.22: Schematic of a cooling tower. The entropy that is rejected by the power plant (I_{S1}) has to be communicated to the environment.

Assume the power plant is designed to eject a current of entropy I_{S1} to the cooling water. At least this amount of entropy will have to be carried away by the moisturized air leaving the cooling tower.

We can calculate the performance of a cooling tower using the type of (steady-state) model discussed above and applied in Example 15.6 and Example 15.7. To exercise a less formal approach, consider the following simplified model that is suitable for estimates. The entropy coming from the power plant (I_{S1}) has to be communicated to the environment (I_{S2}). If we assume the entropy current leaving the cooling tower with the humid air to be equal to the one from the power plant, we neglect entropy production in the tower and the entropy current with makeup water. (Entropy production is mostly due to mixing of water, vapor, and air at different conditions, and the dissipation of the energy used for pumping, which is neglected here anyway.)

If we assume further that the temperature of the air flowing though the cooling tower does not change much, its entropy will not either. Therefore, all the entropy communicated to the tower from the power plant has to be in the water that is evaporated and added to the airflow:

$$I_{S2} = \left(s_{v2}\omega_2 - s_{v1}\omega_1\right) I_{ma} \tag{15.52}$$

This is so because ωI_{ma} is the current of water vapor in air if I_{ma} is the current of dry air (Equ.(15.20)). s_v denotes the specific entropy of vapor at its temperature and (partial) pressure. If we specify the condition of the air at the inlet and outlet of the cooling tower, we can calculate the humidity ratios according to what we have learned in the previous sections. Calculating the entropies poses a small problem. Equ.(15.52) shows that we cannot just work with the difference of the entropies at two states. To deal with this case properly, we have to make sure we have the entropy with respect to a well defined state that holds for both points 1 and 2. This can be insured by setting the entropy of liquid water equal to zero at $T = 273$ K and $P = 101.3$ kPa. The entropy of the vapor can be calculated from this if the entropy of vaporization and the temperature coefficient of enthalpy of the vapor are known (Example 15.9).

QUESTIONS

9. What kind of reasoning leads to the expression in Equ.(15.35)?
10. Why are the fluxes in the model of Fig. 15.19 spatially constant (independent of z)?
11. Why does the current of vapor in evaporation inside a container depend upon the ratio of the pressures of the dry air far from the water and near its surface?
12. If hot dry air is cooled by evaporating some water (as in Fig. 15.20), what happens to the exit temperature of the stream of air if the flow of water is increased? Do you expect there to be a minimum of entropy production for some water current, or does the entropy production rate vary monotonically?
13. Why is it possible to neglect entropy production in the model shown in Fig. 15.21
14. What are the conditions necessary for the entropy current leaving a cooling tower to be equal to the one rejected by the power plant? Where do you expect these conditions to be violated most strongly?

EXAMPLE 15.7. Cooling air by humidification.

Hot (40°C) dry ($\phi = 0.1$) air flows through an evaporative cooler as in Fig. 15.20. The current of mass of the air alone is 1.0 kg/s. How much water needs to be added each second to cool the air to 28°C? (The water added has a temperature of 25°C) What will the relative humidity of the air at that point be? Ambient pressure is taken to be 1.0 atm.

SOLUTION: We formulate the laws of balance of energy and mass, the constitutive relations, and the properties of the substances in EES (Klein et al., 1991). The laws of balance take the forms

```
ha_T1*I_ma_1 + hg_T1*I_mv_1 + hw_Tw*I_mw_1 =
                    ha_T2*I_ma_2 + hg_T2*I_mv_2
I_ma_2 = I_ma_1
I_mv_2 = I_mv_1 + I_mw_1
```

The constitutive relation needed are

```
Pv_T1 = phi_1*Pg_T1
w_1 = 0.622*Pv_T1/(P1-Pv_T1)
I_mv_1 = w_1*I_ma_1
w_2 = I_mv_2/I_ma_2
Pv_T2 = w_2/(w_2 + 0.622)*P1
phi_2 = Pv_T2/Pg_T2
```

and the pressures and enthalpies can be evaluated with the help of

```
Pg_T1 = Pressure(Steam,T=T1,X=1)     ha_T1 = Enthalpy(Air,T=T1)
hg_T1 = Enthalpy(Steam,T=T1,X=1)     ha_T2 = Enthalpy(Air,T=T2)
hg_T2 = Enthalpy(Steam,T=T2,X=1)     hw_Tw = Enthalpy(Steam,T=Tw,X=0)
```

Pg_T2 = Pressure(Steam,T=T2,X=1)

If we now define the given quantities:

phi_1 = 0.1	T1=40	Tw = 25
P1=101.3	I_ma_1 = 1	T2 = 28

the model can be solved. It turns out that we need a current of water of 5.0 g/s to achieve the stated goal. The relative humidity of the cooler air will be 0.405.

EXAMPLE 15.8. Parameters for mass and entropy transfer in evaporative cooling of water.

Use the results of the experiment shown in Fig. 15.21 to estimate (a) the conductivity for mass for the evaporative process, and (b) the overall entropy conductivity of the container.

SOLUTION: (a) Consider the situation after $t = 15000$ s when the processes have almost reached steady-state conditions. The first diagram in Fig. 15.21 shows that the current of mass is almost constant at a value of roughly (0.184 – 0.165) kg / 20000 s = $9.5 \cdot 10^{-7}$ kg/s. To determine the mass conductivity, we use Equ.(15.50)

$$G_{m,v} = -\frac{I_{m,v}}{\phi P_g(T_a) - P_g(T_w)} = -\frac{9.5 \cdot 10^{-7}}{0.15 \cdot 2550 - 1700}\frac{\text{kg}}{\text{s} \cdot \text{Pa}} = 7.2 \cdot 10^{-10}\frac{\text{kg}}{\text{s} \cdot \text{Pa}}$$

The humidity was 0.15, and the temperatures of air (21.5°C) and of water (15°C) were read from the diagram at the center of Fig. 15.21. Saturated vapor pressures were taken from Table 15.1.

(b) If we use the steady-state version of the law of balance of entropy for the water as expressed by the diagram on the right in Fig. 15.21, i.e.,

$$I_{S,cond} = I_{S,evap}$$

we can find the overall entropy conductivity from the water to the environment. We need to introduce constitutive relations in the law of balance:

$$G_S(T_a - T_w) = s_{vap}(T_w) I_{m,v}$$

which leads to

$$G_S = \frac{s_{vap}(T_w) I_{m,v}}{T_a - T_w} = \frac{8780 \cdot 9.5 \cdot 10^{-7}}{21.5 - 15}\frac{\text{W}}{\text{K}^2} = 1.3 \cdot 10^{-3}\frac{\text{W}}{\text{K}^2}$$

The specific entropy of the vapor has been taken from Table 15.1.

EXAMPLE 15.9. Estimating evaporation in a cooling tower.

Use the strongly simplified model of a cooling tower that led to Equ.(15.52) in order to find the flow of cooling water, the current of air and the amount of water evaporated for the following thermal power plant. Calculate the fraction of water that has to be resupplied (makeup water).

The plant has an electric power of 260 MW. The endoreversible part operates between 300°C and 40°C. The cooling water circulating through the tower arrives with a temperature of 40°C and returns to the condenser at 25°C. The temperature and humidity of the incoming air are 25°C and 20%, respectively; for the outgoing air they are 30°C and 90%.

SOLUTION: We first calculate the entropy current emitted by the (endoreversible part of the) engine. For a power of 240 MW and a temperature drop of 260 K, the current of entropy is

$$I_{S1} = \mathcal{P}/\Delta T = 260 \cdot 10^6 / 260\,\mathrm{W/K} = 1.0 \cdot 10^6\,\mathrm{W/K}$$

If we assume that the entropy can be communicated to the cooling water without dissipation, the current of cooling water is calculated from

$$I_{S1} = c_{pw} \ln\left(T_3/T_6\right) I_{mw}$$

$$I_{mw} = \frac{I_{S1}}{c_{pw}\ln\left(T_3/T_6\right)} = \frac{1.0 \cdot 10^6}{4200 \cdot \ln\left(313/298\right)}\frac{\mathrm{kg}}{\mathrm{s}} = 4850\frac{\mathrm{kg}}{\mathrm{s}}$$

The state of the air at the inlet and outlet to the cooling tower allows us to calculate the vapor pressures:

$$P_{v1} = \phi_1 P_g\left(T_1\right) = 0.20 \cdot 3.17\,\mathrm{kPa} = 0.634\,\mathrm{kPa}$$

$$P_{v2} = \phi_2 P_g\left(T_2\right) = 0.90 \cdot 4.25\,\mathrm{kPa} = 3.82\,\mathrm{kPa}$$

Saturated vapor pressures have been taken from Table 15.1. Now we estimate the (specific) entropy of vapor using the ideal gas model and the reference state T_{ref}, $P_{v,ref}$:

$$s_v\left(T, P_v\right) = s_{v,ref} + c_{pv}\ln\left(\frac{T}{T_{ref}}\right) - \frac{R}{M_0}\ln\left(\frac{P_v}{P_{v,ref}}\right)$$

Here, c_{pv} = 1870 J/(K · kg) is the specific temperature coefficient of enthalpy of water vapor (it depends slightly upon temperature). T_{ref} = 273, and $s_{v,ref}$ and $P_{v,ref}$ are determined as follows. We set the entropy of liquid water equal to zero at 273 K. At this temperature, it takes about 9160 J/K of entropy to evaporate 1 kg of water which then ends up at a pressure of 0.61 kPa (see Table 15.1). Therefore,

$$s_{v,ref} = 9160\,\mathrm{J}/\left(\mathrm{K} \cdot \mathrm{kg}\right) \quad , \quad T_{ref} = 273\,\mathrm{K} \quad , \quad P_{v,ref} = 0.610\,\mathrm{kPa}$$

This model yields pretty good results when compared to values found in Table 15.1. Using this determination, the specific entropies at points 1 and 2 turn out to be equal to s_{v1} = 9310 J/(K · kg) and s_{v2} = 8510 J/(K · kg), respectively.

To find the current of mass of dry air necessary for making the operation of the cooling tower possible, we use Equ.(15.52) together with Equ.(15.21):

$$I_{S2} = 0.622\left(s_{v2}\frac{P_{v2}}{P - P_{v2}} - s_{v1}\frac{P_{v1}}{P - P_{v1}}\right) I_{ma}$$

Setting $I_{S2} = I_{S1}$ and plugging in values yields a result of I_{ma} = 5900 kg/s. This allows us to calculate the currents of water vapor at points 1 and 2 (23 kg/s and 143 kg/s) from which we find the rate at which water has to evaporate, namely, 120 kg/s. This equals 2.0% of the cooling water. [These estimates are pretty good. A model based on the balance of energy—which implicitly includes dissipation—using actual property values yields 5500 kg/s for the current of cooling water, and a rate of evaporation of 112 kg/s.]

15.4 VAPOR POWER AND REFRIGERATION CYCLES

In this last section of this chapter we will be dealing mostly with engineering applications of the thermodynamics of fluid systems, i.e., with vapor power cycles and refrigeration systems.[2]

Fluid processes which include phase changes will allow us to apply what we have learned about pure ideal fluids in Section 15.1 and Section 15.2, and to combine the information with ideas discussed in the parts on fluid flow (mainly Chapter 8). In practical applications, fluids which can be treated as pure, run through cyclic processes while flowing through different parts of an engine, such as compressors or turbines, pumps or throttles, and so on. In contrast to what we discussed earlier, the fluids will be allowed to evaporate and to condense at various stages of the cycles.

15.4.1 Property Data and the Computation of Processes

If you want to calculate processes of simple fluids undergoing temperature and pressure changes, and phase changes and mixing, you will need detailed information about the properties of the substances involved. These properties are reported in the form of tables or graphs, of which the steam tables for water are the most famous. Even though you can also take advantage of computer programs providing the information in function format,[3] it helps to look at the actual numbers when you learn about the subject. An overview of the three main segments of fluid states is shown in Fig. 15.23 (see also Fig. 15.5). Table 15.1 provides values for saturated water (liquid or vapor; mixtures are calculated from the values of the saturated fluids). Also, if you wish to be able to calculate changes in the region of the superheated vapor, appropriate tables have to be available (see Table 15.3 and Figures 15.28 and 15.29). Properties of subcooled or compressed liquid water complete the list of necessary materials (Fig. 15.25).

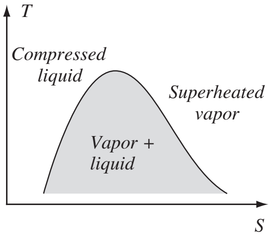

Figure 15.23: Compressed (subcooled) liquid, superheated steam, and mixtures of vapor and liquid are the main forms of a pure fluid.

Saturated fluids. To orient ourselves to the properties of fluids, it is convenient to start with the state of saturation, since the *saturation line* naturally divides the domain of independent variables into the different sections discussed above. The transition from the liquid to the gaseous state of a fluid is outlined in the *TS* diagram. To catch this transition, one computes the values of thermodynamic properties of the saturated fluid, i.e., of saturated liquid and saturated vapor. We have seen what distinguishes the saturated fluid (and mixtures of the phases) from the rest: it is the nature of the chemical potential at those particular conditions. As we have learned during the description of phase changes, the chemical potential remains unchanged. Therefore, the potential is the same for both the liquid and the vapor at a given temperature.

The chemical potential of both phases is listed in the third column in Table 15.1. As you can show by directly calculating the potential using energy, volume, and entropy, its values are indeed equal for the liquid and the vapor:

$$u_l + P\upsilon_l - T s_l = u_g + P\upsilon_g - T s_g \qquad \textbf{(15.53)}$$

Continuing with Table 15.1, the second column reports the vapor pressure of the fluid, while the last six columns list entropy, specific volume, and specific energy of both the liquid and the vapor. The values are given on a mass basis (specific values).

So far, we have used the *TS* diagram only for reporting fluid properties, but other diagrams are used as well. In Fig. 15.24, the distinctive saturation curve is presented for the refrigerant R123. The information is given in the *TS* and the pressure-enthalpy di-

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[2] For more information, see Moran and Shapiro (1992), or Cengel and Boles (2002).

[3] See EES (Klein et al., 1991).

agrams. Depending on your purpose, you might use either diagram to discuss vapor processes.

Table 15.3: Properties of superheated water vapor[a]

	0.3 bar			1.0 bar			3.0 bar		
T / °C	s	v	e	s	v	e	s	v	e
80	7.8282	5.4015	2483.8						
120	8.0358	6.0273	2542.4	7.4665	1.7931	2537.0			
160	8.2229	6.6485	2601.0	7.6591	1.9838	2597.5	7.1274	0.6506	2586.9
200	8.3944	7.2676	2660.1	7.8335	2.1723	2657.6	7.3108	0.7163	2650.2
240	8.5535	7.8855	2719.9	7.9942	2.3594	2718.1	7.4765	0.7804	2712.6
280	8.7021	8.5026	2780.7	8.1438	2.5458	2779.2	7.6292	0.8438	2775.0
320	8.842	9.1193	2842.3	8.2844	2.7317	2841.1	7.7716	0.9067	2837.8
360	8.9743	9.7356	2904.9	8.4171	2.9173	2904.0	7.9057	0.9692	2901.2
400	9.1001	10.3518	2968.5	8.5432	3.1027	2967.7	8.0327	1.0315	2965.4
440	9.2201	10.9677	3033.2	8.6634	3.2879	3032.5	8.1536	1.0937	3030.5
480	9.3349	11.5836	3098.9	8.7785	3.4730	3098.3	8.2692	1.1557	3096.6
520	9.4452	12.1994	3165.7	8.8889	3.6581	3165.2	8.3800	1.2177	3163.7

[a] Units as in Table 15.1.

	10 bar			30 bar			100 bar		
T / °C	s	v	e	s	v	e	s	v	e
200	6.6932	0.2059	2621.5						
240	6.8805	0.2274	2692.2	6.2251	0.0682	2618.9			
280	7.0454	0.2479	2759.6	6.4445	0.0771	2709.0			
320	7.1954	0.2678	2825.6	6.6232	0.0850	2787.6	5.7093	0.0192	2588.2
360	7.3344	0.2873	2891.3	6.7794	0.0923	2861.3	6.0043	0.0233	2728.0
400	7.4648	0.3066	2957.2	6.9210	0.0994	2932.7	6.2114	0.0264	2832.0
440	7.5882	0.3257	3023.6	7.0521	0.1062	3003.0	6.3807	0.0291	2922.3
480	7.7055	0.3447	3090.6	7.1750	0.1129	3073.0	6.5287	0.0316	3005.8
520	7.8177	0.3635	3158.5	7.2913	0.1195	3143.2	6.6625	0.0339	3085.9
560	7.9254	0.3823	3227.2	7.4022	0.1260	3213.8	6.7862	0.0362	3164.0
600	8.0292	0.4011	3297.0	7.5084	0.1324	3285.0	6.9022	0.0384	3241.1
640	8.1293	0.4198	3367.7	7.6105	0.1388	3357.0	7.0119	0.0405	3317.9

Subcooled (compressed) liquid. If a fluid exists in liquid form only, it may either satisfy the special condition of saturation (in which case its states would be found on the saturation line in Fig. 15.23), or it may be found in the subcooled (compressed) region. Since liquids are hard to compress, their condition usually does not deviate much from that of the saturated liquid, if the pressure is not too high. Fig. 15.25 shows a small region of the *TS* diagram of water near the liquid saturation line. It demonstrates that, for a pressure of 300 bar, the temperature is larger by only about 5 K if the entropy is held constant. Put differently, for pressures in the range of up to a few hundred bar, the states lie in a narrow band around the saturation line. Entropy, energy, and volume of the liquid may be approximated by the saturated liquid data for the desired temperature, independently of pressure. Enthalpy, on the other hand, can be given by

$$h(T,P) = h_l(T) + (P - P_l)\upsilon(T) \qquad \textbf{(15.54)}$$

where the index *l* refers to the state of liquid saturation.

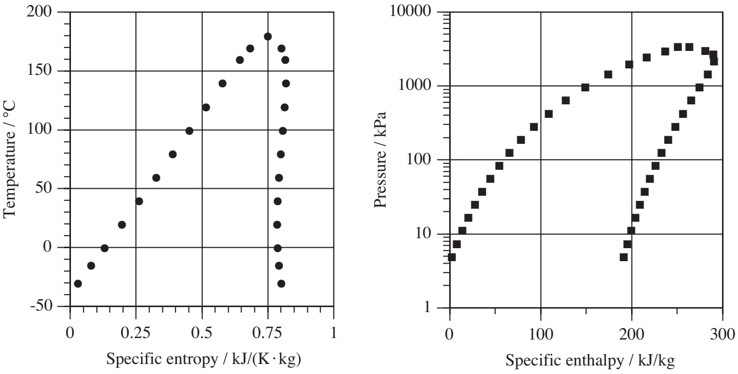

Figure 15.24: The saturation line for the refrigerant R123 looks quite different from that of water. While in the case of water, vapor will condense if it is compressed isentropically, this does not always happen with R123. (Consider, for example, a process starting with the saturated state at a temperature of 100°C, and leading to one at a lower temperature.) The curves have been computed using the program EES (Klein et at., 1991).

Note that, under these conditions, the lines of constant enthalpy are nearly horizontal, meaning that this quantity is constant for constant temperature.(We can draw the same

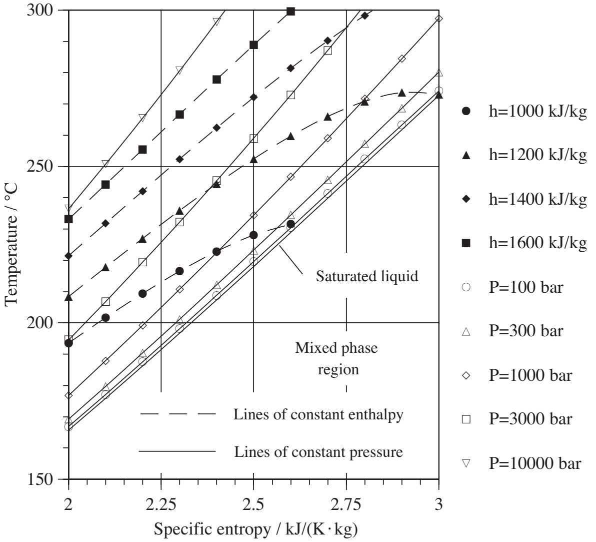

Figure 15.25: A small segment of the *TS* diagram of subcooled water. For pressures that are not too large, the state of water is well approximated by that of the saturated liquid. At very high pressures, deviations become increasingly important. The diagram shows lines of constant pressure and enthalpy. Computations were done using the program EES (Klein et at., 1991).

conclusion from the equation above for small specific volume and pressures that are not too large.) This is what we would expect of an incompressible substance. Take a closer look at the model of an *incompressible fluid*. Such a fluid is commonly defined as one having a constant specific volume, and whose energy depends only upon temperature. The enthalpy is then given by

$$h(T,P) = u(T) + P\upsilon \tag{15.55}$$

Under these circumstances, the temperature coefficient of energy (the specific heat at constant volume) is a function of temperature only, and the temperature coefficient of enthalpy (i.e., the specific heat at constant pressure) must be equal to the former:

$$\begin{aligned} c_V(T) &\equiv \frac{\partial u(T)}{\partial T} = \frac{du}{dT} \\ c_P(T) &\equiv \frac{\partial h(T,P)}{\partial T} = \frac{du}{dT} \end{aligned} \tag{15.56}$$

Changes of energy and of enthalpy are obtained by integrating the appropriate expressions. For constant coefficients, the results take the form

$$\begin{aligned} u(T) &= u(T_0) + c(T - T_0) \\ h(T) &= h(T_0) + c(T - T_0) + (P - P_0)\upsilon \end{aligned} \tag{15.57}$$

The same arguments applied to the entropy of the incompressible fluid yield the result, which again holds for constant c:

$$s(T) = s(T_0) + c\ln\left(\frac{T}{T_0}\right) \tag{15.58}$$

These are all relations we have used before in applications. In summary, to compute property data for the compressed liquid, we may use data of the saturated liquid for a desired temperature, and adjust the enthalpy for pressure as in Equ.(15.54). Changes in temperature are taken into account according to the equations given above.

Mixtures of liquid and vapor: the quality. The conditions for which mixtures of a liquid and its vapor exist need special attention. It is customary to describe the properties in terms of the composition of the mixture, which is quantified by stating how much vapor is present relative to the total fluid:

$$x = \frac{n_g}{n_l + n_g} = \frac{m_g}{m_l + m_g} \tag{15.59}$$

This quantity is called the *quality* of the mixture (Fig. 15.26). Note that it is equivalent to the notion of the mole fraction (of vapor) of a two-component mixture. All the intermediate states of the mixed fluid (liquid plus vapor) can be computed on the basis of the values of the saturated fluid. This means that we do not need additional data for this set of conditions. A fluid with a quality of 0 or 1 simply corresponds to pure liquid or pure vapor, respectively. States with a quality between these values are found on the horizontal line in the *TS* diagram connecting the conditions of liquid and vapor. (See Fig. 15.27.)

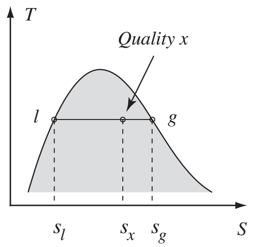

Figure 15.26: A state of quality x and the corresponding pure states (liquid and vapor).

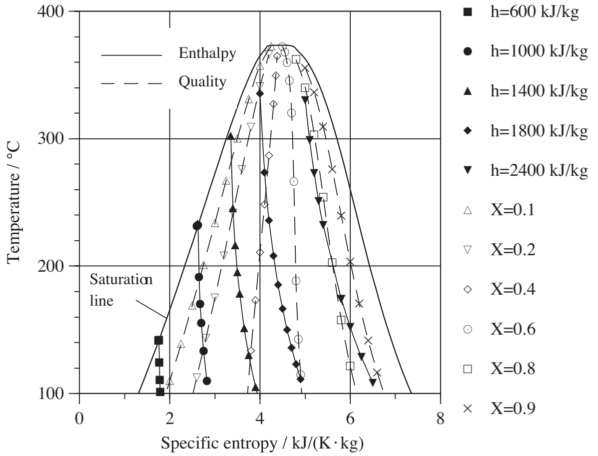

Figure 15.27: Lines of constant enthalpy and of constant quality for the mixed phase states of water. Changes taking place at constant enthalpy include throttling processes (Section 8.6).

The total volume, entropy, energy, and enthalpy of the fluid mixture are expressed as the sum of the corresponding quantities for the liquid and the vapor. To start with the volume, the total specific volume is defined as the total volume divided by the total mass

$$\begin{aligned} \upsilon &= \frac{V}{m} = \frac{V_l + V_g}{m} = \frac{m_l \upsilon_l + m_g \upsilon_g}{m} \\ &= \frac{m_l}{m} \upsilon_l + \frac{m_g}{m} \upsilon_g \end{aligned}$$

which is equivalent to

$$\upsilon = (1 - x)\upsilon_l + x\upsilon_g \tag{15.60}$$

Exactly the same forms can be shown to apply to the other properties:

$$\begin{aligned} s &= (1 - x)s_l + x s_g \\ e &= (1 - x)e_l + x e_g \\ h &= (1 - x)h_l + x h_g \end{aligned} \tag{15.61}$$

Note that the values of s_l and s_g, for example, are those of the saturated states, which correspond to points on the saturation curve of Fig. 15.26. With this information, the values corresponding to any mixture of liquid and vapor can be computed.

Superheated vapor (steam). When we finally have pure vapor, the conditions of the fluid can be changed quite drastically with relatively modest changes of pressure and temperature. This is demonstrated in Fig. 15.28, which shows the part of the *TS* diagram of water to the right of the saturation line. The most important feature of the data presented in the figure is this: vapor can be treated as an ideal gas only if the pressure is not too high. The conditions for which the ideal gas model applies are marked by the horizontal sections of the lines of constant enthalpy. As you remember, this model requires the enthalpy of the fluid to be a function of temperature only. If the conditions of the ideal gas are satisfied, we can apply all the simple relations derived in the previous sections and chapters. Fig. 15.29 indicates that water vapor contained in the atmosphere can be treated in this simple manner. This simplifies applications in atmospheric physics and air conditioning to a certain degree. In the realm of the "real" gases, however, detailed property data, again in the form of tables, graphs, or computer programs, have to be provided (Table 15.3). Calculations by hand are tedious but instructive, at least during the learning phase. Sketching processes in diagrams, however, always helps in visualizing the appropriate information.

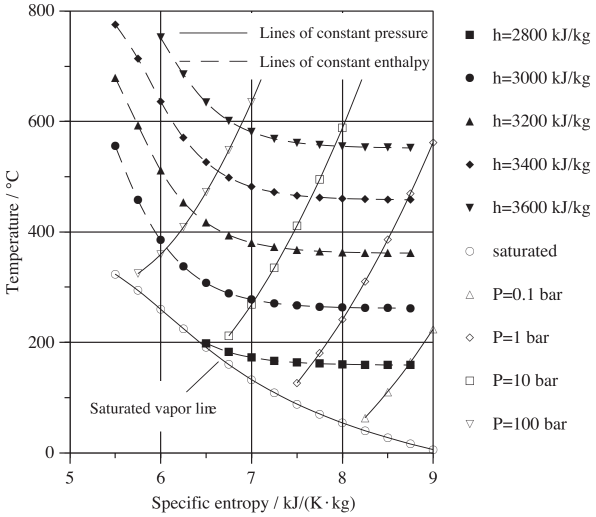

Figure 15.28: Superheated vapor region of the *TS* diagram provides data about the vapor state of the fluid. Lines of constant pressure and enthalpy are given. Where the lines of constant enthalpy are horizontal, we can consider the vapor to be in the ideal gas state. Computations were done using the program EES (Klein et at., 1991).

Calculating processes including phase transitions. Pure fluids that are allowed to go through phase changes play an important role in the sciences and in engineering. So far, we have a theory of uniform reversible processes, as discussed in the previous section. Even though real cases hardly ever conform to the conditions of this model,

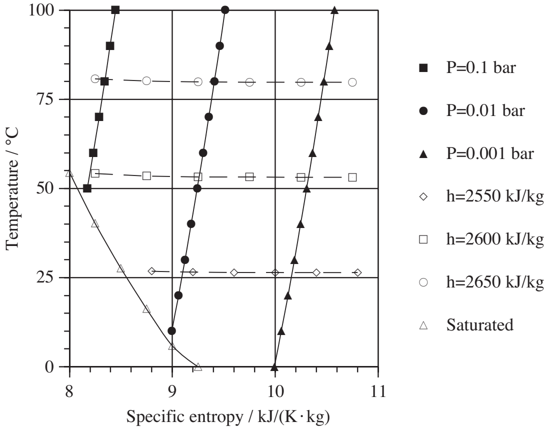

Figure 15.29: Superheated water vapor in the range interesting for moist air here on Earth. The ideal gas model may be applied to the computation of the properties of the water vapor contained in the air.

its results can still be applied. As long as we can provide information about the values of some variables at certain states, changes occurring between those states can be computed for the fluid even if irreversibilities are present. In the absence of more detailed information about actual processes, it is important to be able to approximate them by simple models. Experience shows that the results derived provide for a good basis from which to discuss of concrete cases in engineering and the sciences.

15.4.2 Vapor Power Cycles

Detailed fluid properties play an important role in the design of power plants which use vapor power cycles such as the steam power plant of Fig. 15.30. The thermal part of the plant consists of a boiler, turbine, condenser, and feedwater pump. A fluid such as water circulates through the boiler where steam is produced (points 1 to 2 in Fig. 15.30). Then the steam drives the turbine (points 2 to 3) and enters the condenser, where it is turned into liquid water (points 3 to 4). The feedwater pump increases the pressure of the fluid to the value at the inlet to the turbine (points 4 to 1), completing the cycle.

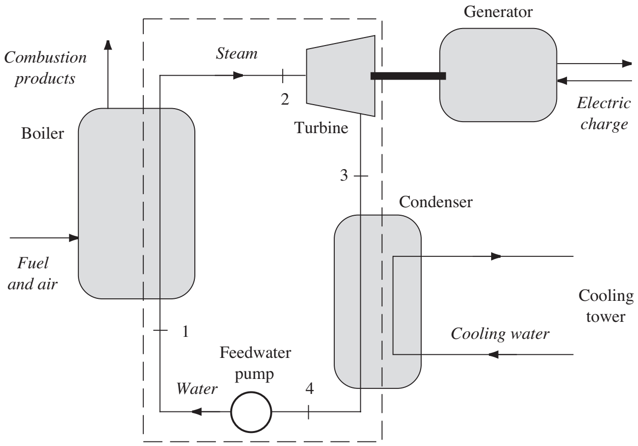

Figure 15.30: Steam power plant. Four devices operate on the water. The feedwater pump increases the pressure of the cold water. This water is then heated and evaporated in the boiler. Steam at high pressure drives the turbine and is thereby expanded adiabatically. Finally, the condenser turns the low pressure steam into water. The dashed line is the surface of the system that encloses the fluid operating in the power plant.

Principle of operation of a steam power plant. We can model the cycle undergone by the fluid as a sequence of steps that we have studied before. First consider each step to be reversible. Starting with the process in the boiler, liquid water at high pressure (P_1) is first heated and then evaporated; assume the step to be finished when all the water is turned into saturated vapor (point 2 in Fig. 15.31). We shall learn later about the consequences of superheating for the vapor power cycle. The step leading from point 1 to point 2 is supposed to take place at constant pressure ($P_2 = P_1$). A simplified model of what happens to the fluid expresses the energy current of heating in the boiler as follows:

$$\left|I_{E,12}\right| \approx \left(\frac{1}{2}\left(T_1 + T_2\right)\left(s_{2'} - s_1\right) + T_2\left(s_2 - s_{2'}\right)\right)I_m \tag{15.62}$$

I_m is the current of mass of the fluid flowing through the main loop of the power plant, and T_1 can be approximated by T_4. (The feedwater pump does not strongly increase the temperature of liquid water.) The upper and the lower temperatures of the cycle are determined by the pressure associated with the appropriate point. Alternatively, the first term in Equ.(15.62) can be computed using the enthalpy of the fluid.

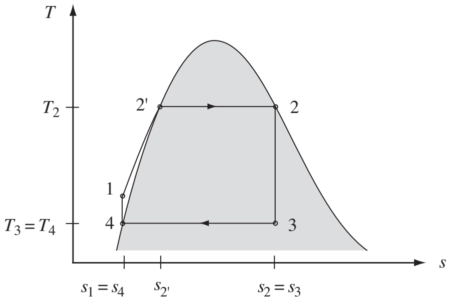

Figure 15.31: Vapor cycle undergone by an ideal fluid in a steam power plant.The sequence of steps is called the *ideal Rankine cycle*.

The second step of the cycle, from point 2 to point 3, is taken to be an isentropic (adiabatic and reversible) expansion of the fluid. According to Fig. 15.31, the quality of the steam leaving the turbine is less than 1, which means that droplets of water form in the turbine. This effect can easily lead to problems with operating the engine. Therefore one tries to keep the quality as high as possible, which can be achieved by superheating the steam (see below). The energy released in this step is transferred to the electric generator of the power plant; it can be calculated either directly or indirectly by calculating the other rates of energy transfer in the cycle.

The condenser, which is basically a heat exchanger operating at constant pressure, turns the steam which has not already condensed, into liquid water. Here, all the entropy added to the cycle in heating is removed and transferred to the environment through a cooling tower or similar device. The rate of energy transfer is easily calculated to be equal to

$$\left|I_{E,34}\right| = T_3\left(s_3 - s_4\right)I_m \qquad \textbf{(15.63)}$$

The final step from point 4 back to point 1 consists of raising the pressure of the liquid to its upper value. The pump is supposed to operate reversibly and adiabatically. Since the density of the liquid usually does not change appreciably, the energy current necessary for operating the pump is computed as follows:

$$\left|I_{E,41}\right| \approx v_4\left(P_1 - P_4\right)I_m \qquad \textbf{(15.64)}$$

Overall, the current of energy delivered by the power plant is calculated from a steady state balance of energy for the system within the dashed line in Fig. 15.30:

$$\begin{aligned}\left|I_{E,23}\right| &= \left|I_{E,12}\right| - \left|I_{E,34}\right| - \left|I_{E,41}\right| \\ &\approx \left(h_{2'} - h_1 + T_2\left(s_2 - s_{2'}\right) - T_3\left(s_3 - s_4\right) - v_4\left(P_1 - P_4\right)\right)I_m\end{aligned} \qquad \textbf{(15.65)}$$

Superheating in the power cycle. If heating of the fluid in the boiler is not stopped at the point where all the liquid has turned into saturated vapor, the cycle depicted in Fig. 15.31 changes as demonstrated in Fig. 15.32. The superheating is done in a heat exchanger separate from the boiler, called the superheater. The boiler and superheater are known as the steam generator. Superheating has two main effects: first, the average temperature of heating of the fluid is higher than it would be without the additional process, leading to increased efficiency of the steam engine; second, the problem of low quality of the steam leaving the turbine is alleviated. You may even get pure vapor (quality equal to 1) at the exit of the turbine.

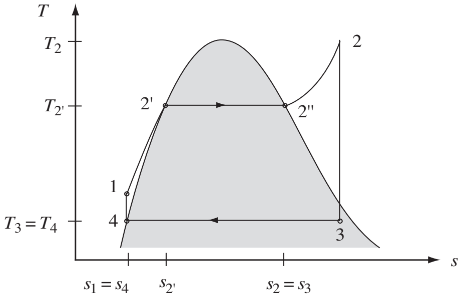

Figure 15.32: Vapor power cycle (ideal Rankine cycle) with superheating of the steam.

Irreversibilities in a vapor power plant. There are numerous sources of entropy production in a vapor power plant. If you look at Fig. 15.30, you can identify different processes leading to irreversibilities. First, there is the case of generation of heat that is normally accomplished by combustion. As you follow the path of entropy through the plant, you next have to consider the effect of the heat exchangers in the boiler and the condenser. In the fluid undergoing the Rankine cycle, entropy production chiefly occurs in the turbine and the pump, with the turbine usually contributing much more strongly. This latter effect is depicted in Fig. 15.33.

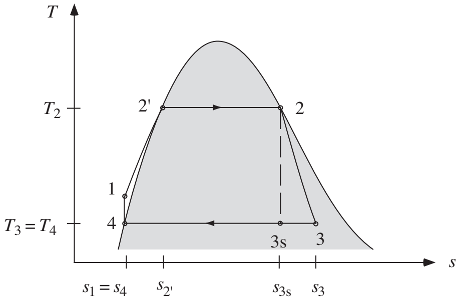

Figure 15.33: Entropy production in the vapor power cycle. The largest contribution to irreversibility in the fluid usually comes from the operation of the turbine.

It is important to consider the rates of entropy production in the entire plant if we wish to quantify the losses occurring as a result of irreversibility (Example 15.13).

15.4.3 Vapor Refrigeration and Heat Pump Systems

Refrigeration and the application of heat pumps to heating systems are two areas where intensive research and development are taking place. The common refrigerants used to date have to be replaced because they are responsible for reducing the ozone layer when released into the environment; and heat pumps have to compete with cheap fossil fuel for a place in heating systems. Finally, in the future, we may wish to replace these sources of energy by those provided directly or indirectly by the Sun, again forcing us to adapt the technical systems.

A vapor Carnot refrigeration or heat pump cycle. We discussed the principle of operation of refrigerators or heat pumps in Chapter 4. There we saw that entropy is pumped from a lower temperature space, using supplied energy, to a higher temperature environment. A simple device for achieving this is a fluid running through a reverse Carnot cycle. If a substance is used which changes its phase in the range of temperatures and pressures encountered, the cycle may look like the one depicted in Fig. 15.34. Starting at point 1, the fluid which has just absorbed the entropy removed from the cold environment, is compressed isentropically to a state corresponding to point 2. Its temperature has therefore changed from the lower value, T_L, to the higher one, T_H. The fluid is then condensed at T_H to form a saturated liquid at state 3, rejecting the entropy it received during the step from point 4 to point 1. To ready the working fluid for picking up entropy again, its temperature must be reduced back to T_L which is achieved by an isentropic expansion to state 4. Finally, the fluid is evaporated while entropy is transferred into it from the cold space. This completes the cycle leading through points 1–2–3–4–1.

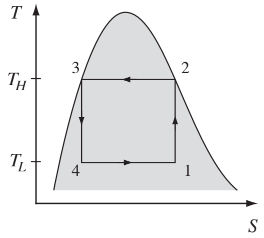

Figure 15.34: Carnot refrigeration cycle in the liquid-vapor region of a fluid. The cycle runs in the opposite direction from a Carnot power process.

A technical realization of the Carnot cycle described uses four elements as shown in Fig. 15.35. We need a compressor to let the fluid undergo the step from point 1 to point 2. As in previous discussions, we first assume the process undergone by the fluid to be reversible; in other words, step 1–2 is a reversible adiabatic compression. Condensation of the high temperature and high entropy fluid takes place at constant pressure and temperature in the condenser, which is in contact with the high temperature environment. During step 2–3, the entropy picked up from the cold environment is rejected to the space at high temperature. The subsequent isentropic expansion requires a turbine which delivers useful energy for driving the compression. Finally, we need an evaporator in contact with the cold space.

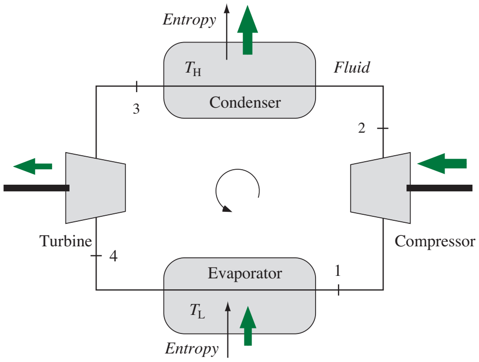

Figure 15.35: Reversible four-step vapor refrigeration cycle requires four components. Evaporator and condenser are in contact with the cold and the warm spaces, respectively. Commonly, the turbine is replaced by a throttling valve as in Fig. 15.36.

A more realistic vapor refrigeration cycle. Even if we could achieve this reversible operation of the Carnot cycle, we would still not realize it in practice for two reasons. First, since the fluid in state 1 is a mixture of liquid and vapor, the presence of liquid droplets might damage the compressor. Therefore, step 1–2 in Fig. 15.34 is replaced by one where we have only vapor (see Fig. 15.36). The latter process is called dry compression, in contrast to the wet compression discussed above.

Second, the turbine normally is left out of the cycle. First of all, step 3–4 delivers only a small amount of energy compared to the energy needed for compression. Additionally, turbines operate rather poorly under the conditions called for in a refrigeration cycle. Therefore, the turbine is replaced by a simple throttling valve; the liquid at point 3 is allowed to expand freely while conserving its specific enthalpy:

$$h_3 = h_4 \tag{15.66}$$

Naturally, this process is irreversible as is step 1–2, under realistic conditions in the compressor (not shown in Fig. 15.36).

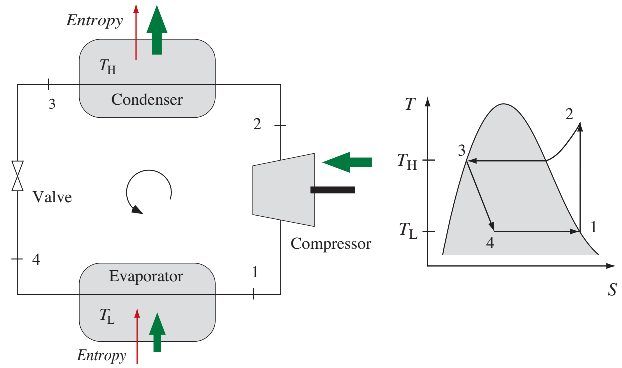

Figure 15.36: A realistic vapor refrigeration cycle includes a throttling valve rather than a turbine for the expansion step. Also, step 1–2 is performed with vapor only, instead of with a mixture of vapor and liquid.

Absorption refrigeration. Energy is needed to raise entropy from a cold space to warmer surroundings. In the refrigeration cycles discussed, this energy is provided during the compression stage of the refrigerator or the heat pump. The compressor needs to be driven mechanically (or electrically) requiring other than thermal energy sources. There is a way, however, to use heat from a high temperature source to drive a refrigeration cycle.

Consider the setup as Fig. 15.37 which provides the technical means for an absorption refrigeration cycle. At point 1, a refrigerant, such as ammonia, leaves the evaporator as vapor. Next, the vapor enters the first of three elements which replace the compressor of a standard refrigerator. This device is an absorber, in which ammonia is absorbed by liquid water to form a strong water-ammonia solution. This step is exothermic, meaning that entropy will be rejected to the environment, requiring a means of cooling the absorber. The liquid solution then enters a pump which increases the pressure of the fluid to the level needed subsequently in the condenser. Since the fluid is a liquid, compressing it requires much less energy than has to be supplied in the compression step of a normal refrigerator. The strong solution leaves the pump at high pressure and enters a generator where a high-temperature source of entropy drives the ammonia out of the solution.

Now the process splits into two paths. The weak solution (essentially water obtained after the ammonia has been driven out) returns to the absorber through a valve which allows for the pressure of the fluid to be reduced to its value in the lower portion of the cycle. Ammonia vapor at high pressure and temperature, on the other hand, enters the condenser, where the entropy picked up from the space to be cooled is rejected to the environment. The vapor finishes its cycle by passing through the throttling valve from point 3 to point 4, and by subsequently flowing through the evaporator where it again absorbs entropy.

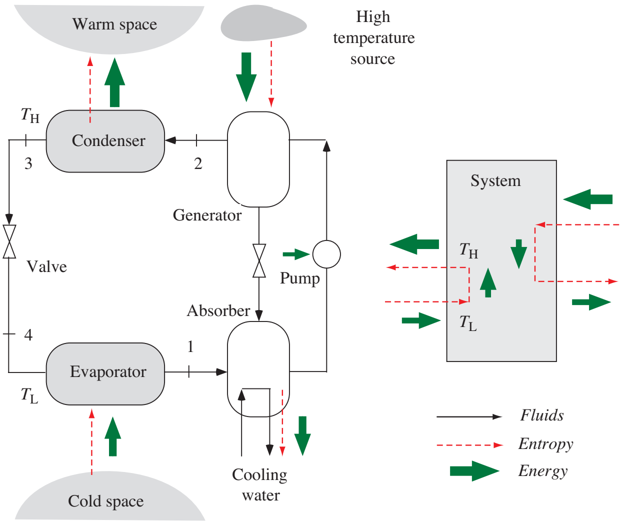

Figure 15.37: In an absorption refrigeration or heat pump system, the energy needed to pump entropy from a cold to a warm space is provided by a thermal process running between a generator and an absorber. In the absorber, the fluid of the refrigeration cycle (ammonia) is absorbed by a liquid (water). In the generator, heat from a high temperature source drives the refrigerant out of the strong solution. The former step is exothermic, while the latter is endothermic. (See also Herrmann, 2009.)

If you consider the thermodynamics of this entire process, you will notice that the energy needed to pump entropy from the cold space to the warmer surroundings is provided by lowering entropy from the high temperature source through the generator to the absorber and into the fluid used to cool the latter device. In effect, we have a “thermal transformer” in analogy to electrical or mechanical transformers (a gear box would provide an example of the latter). The flow diagram in Fig. 15.37 provides an explanation of the process.

Having a means of pumping heat without the need for electrical power allows for refrigeration and heat pump processes to be directly driven by the Sun. Absorption refrigeration has been studied extensively in solar energy engineering. The solar collectors, absorber, pump, and generator, however, may increase the cost of such systems considerably, making them too expensive where electrical power is cheap.

QUESTIONS

15. How are properties of mixtures of liquid and vapor calculated?
16. What is the meaning of the saturation line?
17. Consider an amount of liquid being converted into steam. What can be said about the chemical potential of the mixture of liquid and steam along the horizontal line in 15.26?
18. What does Equ.(15.54) tell us about the chemical potential of a compressed liquid at different pressures for a given temperature?
19. Why is the temperature coefficient of enthalpy of an incompressible fluid equal to the temperature coefficient of energy?
20. What problem can occur in a turbine if the steam flowing in is saturated?
21. Why does step 3-4 in Fig. 15.36 run to the lower right in the *TS* diagram?

EXAMPLE 15.10. The entropy of a mixture of water and water vapor.

Water is found to vaporize at a temperature of 200°C. If there are 12 kg of liquid water and 18 kg of water vapor present, how large is the entropy of the mixture? Estimate the necessary values from Fig. 15.27.

SOLUTION: First, we determine the quality of the mixture of steam and water. It is given by

$$x = \frac{m_{vapor}}{m_{liquid} + m_{vapor}} = \frac{18}{12+18} = 0.60$$

Now we need only the specific entropies of saturated water and of saturated steam at a transitional temperature of 200°C. According to Fig. 15.27, the values are 2300 J/(K · kg) and 6400 J/(K · kg), respectively. Using Equation (201a), we calculate the specific entropy of the mixture to be equal to

$$s = (1-x)s_{liquid} + x\,s_{vapor} = (1-0.6)\cdot 2300 + 0.6\cdot 6400 = 4760\frac{\text{J}}{\text{K}\cdot\text{kg}}$$

With a total mass of 30 kg, the final result is 143 kJ/K.

EXAMPLE 15.11. Energy currents and efficiency of an ideal Rankine cycle.

An ideal Rankine cycle is operated for water at a high pressure of 80 bar and a low pressure of 0.1 bar. Steam is not superheated. (a) With a current of water of 100 kg/s, estimate the energy current with respect to the fluid in the boiler; use the diagrams showing fluid properties provided in this chapter. (b) How large is the energy current leaving the power plant due to cooling? (c) What is the power necessary to operate the feedwater pump? (d) Calculate the thermal efficiency of the cycle. (e) If the water used for cooling the plant enters at a temperature of 20°C and leaves at 35°C, how large does the current of mass of the cooling liquid have to be? (f) Calculate the quality of the fluid after isentropic expansion. (g) If the quality at the end of isotropic expansion is equal to 1, what is the efficiency of the cycle?

SOLUTION: Since you will probably solve the problem by reading property values from the graphs, you will get only approximate results. (Try solving this same problem with values read from tables or computed using appropriate programs.) First consider Fig. 15.4, which has been redrawn in a slightly different manner in Fig. 15.33 and Fig. Ex.11. Both cycles, i.e., those with and without superheating, have been superimposed on the graph below. The former joins the points 1 – 2' – 2" – 3' – 4 – 1, while the latter includes point 2 and 3.

The lines of constant pressure for 0.1 bar, 60 bar, and 150 bar have been included. For the upper pressure of 100 bar, we have to interpolate in the diagram. We can read the following values from this graph and from Figures 15.10 and 15.27 (see Table 15.4 below):

(a) The energy current added to the steam in heating from point 1 to point 2" can be estimated as in Equ.(15.62):

$$\begin{aligned} I_{E,1-2''} &= \left[T_{m,1-2'}\left(s_{l,2'} - s_{l,1}\right) + T_H\left(s_{g,2''} - s_{l,2'}\right)\right] I_m \\ &= \left[450\cdot(3.2-0.7) + 573\cdot(5.7-3.2)\right]\cdot 100\,\text{kW} = 255\,\text{MW} \end{aligned}$$

(b) Condensation takes place at constant temperature from point 3' to point 4:

$$I_{E,3'-4} = T_l\left(s_{g,2''} - s_{l,1}\right) I_m = 323\cdot(5.7-0.7)\cdot 100\,\text{kW} = 162\,\text{MW}$$

(c) The energy current necessary for compressing the liquid from the state at point 4 to the one at point 1 turns out to be rather small:

$$I_{E,4-1} \approx v\left(P_1 - P_4\right) I_m \approx 1.2 \cdot 10^{-3} \cdot 8 \cdot 10^6 \cdot 100\,\mathrm{W} = 1\,\mathrm{MW}$$

Table 15.4: Steam properties at low and high pressure in the cycle

Pressure	$T_{evaporation}$	s_l	s_g
0.1 bar	50°C	0.7 kJ/(K·kg)	
80 bar	300°C	3.2 kJ/(K·kg)	5.7 kJ/(K·kg)

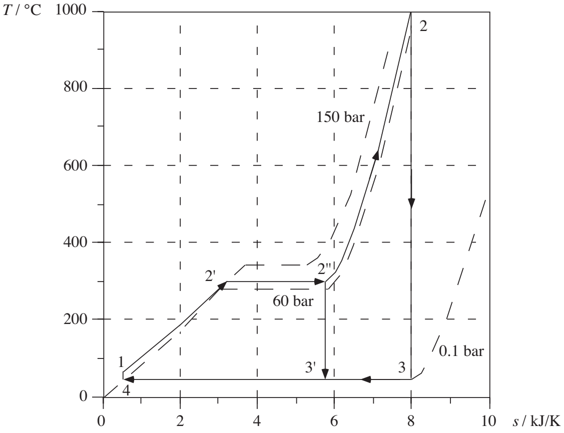

Figure Ex.11

(d) The numbers computed so far let us calculate the thermal efficiency of the plant:

$$\eta = \frac{\left(I_{E,1-2''} + I_{E,4-1}\right) - I_{E,3'-4}}{I_{E,1-2''} + I_{E,4-1}} = \frac{256 - 162}{256} = 0.37$$

(e) The entire energy current discharged in the condenser must be carried away by the cooling water. For this fluid, we can assume conditions of constant pressure and constant temperature coefficient of enthalpy. Therefore we have

$$c_P I_{m,cooling}\left(T_{c,\mathrm{H}} - T_{c,\mathrm{L}}\right) = I_{E,3'-4} \quad \Rightarrow \quad I_{m,cooling} = 2570\,\mathrm{kg/s}$$

(f) By extrapolating the lines of constant quality in Fig. 15.27 down to a temperature of 50°C, we obtain a value of $x = 0.7$ for the quality of the vapor at point 3'.

(g) To answer this question, we have to recalculate the quantities obtained above, this time including superheating of the steam from point 2" to point 2. The important quantity to be read from the graph is the specific entropy of 8.0 kJ/(K·kg) at a temperature of about 1000°C at point 2. Estimates of the additional or new energy currents are

$$I_{E,2''-2} = T_{m,2''-2}\left(s_{g,2''} - s_{g,2}\right) I_m = 923 \cdot (8.0 - 5.7) \cdot 100\,\mathrm{kW} = 210\,\mathrm{MW}$$

$$I_{E,3-4} = T_l\left(s_{g,2'} - s_{l,1}\right) I_m = 323 \cdot (8.0 - 0.7) \cdot 100\,\mathrm{kW} = 236\,\mathrm{MW}$$

The new thermal efficiency turns out to be ((256+210)–236)/(256+210) = 0.49.

EXAMPLE 15.12. Entropy production and efficiency of a turbine.

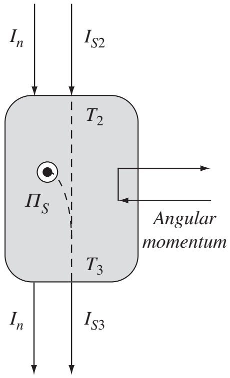

Figure Ex.12

The isentropic efficiency of a turbine is defined as the ratio of its actual power and the power it would have if it were operated isentropically. (a) Draw a flow diagram for the operation of the turbine. (b) Derive an expression for the rate of entropy production of the turbine in terms of the efficiency, the enthalpies of the fluid at points 2 and 3*s* in Fig. 15.33, and the current of mass of the fluid.

SOLUTION: (a) According to the discussion of flow processes in Chapter 8, the flow diagram including the effect of irreversibility must look as shown in Fig. Ex.12. While the current of amount of substance is constant, the flux of entropy increases because of irreversibility.

(b) The energy current associated with the mechanical process of the turbine can be calculated as the difference of the energy fluxes entering and leaving the system together with the steam. According to Section 8.3, the latter currents can be written in terms of the flux of amount of substance, the chemical potentials, and the molar entropies:

$$\begin{aligned}\left|I_{E,mech}\right| &= \left|I_n\right|\left[\left(\mu_2 + T_2\bar{s}_2\right) - \left(\mu_3 + T_3\bar{s}_3\right)\right] = \left|I_n\right|\left[\left(\mu_2 + T_2\bar{s}_2\right) - \left(\mu_3 + T_3\left(\bar{s}_2 + \frac{1}{I_n}\Pi_S\right)\right)\right] \\ &= \left|I_n\right|\left[\left(\mu_2 + T_2\bar{s}_2\right) - \left(\mu_3 + T_3\bar{s}_2\right)\right] - T_3\Pi_S\end{aligned}$$

The term multiplying the current I_n is equal to the difference of the molar enthalpies of the fluid at points 2 and 3*s* in Fig. 15.33. Therefore we have

$$\begin{aligned}\left|I_{E,mech}\right| &= \left|I_n\right|\left[\bar{h}_2 - \bar{h}_{3s}\right] - T_3\Pi_S \\ &= \left|I_m\right|\left[h_2 - h_{3s}\right] - T_3\Pi_S\end{aligned}$$

While the quantity on the left-hand side is the real power of the turbine, the first term on the right is the isentropic power. With the definition

$$\eta_{turbine} = \left|I_{E,mech}\right| / \left|I_{E,mech}\right|_S$$

we can express the rate of production of entropy as follows:

$$\begin{aligned}T_3\Pi_S &= \left|I_{E,mech}\right|_S - \left|I_{E,mech}\right| = \left|I_{E,mech}\right|_S - \eta_{turbine}\left|I_{E,mech}\right|_S \\ &= \left(1 - \eta_{turbine}\right)\left|I_m\right|\left[h_2 - h_{3s}\right]\end{aligned}$$

EXAMPLE 15.13. Contributions to irreversibility in a steam power plant.

Consider a power plant running a vapor cycle as described in Example 15.11 (without superheating). Allow for the adiabatic expansion in the turbine to be irreversible. Additional information is provided about the situation in the heat exchangers and in the burner. Calculate the relative importance of the different sources of irreversibility. (a) Assume that methane is burned as fuel using the theoretical amount of air. The hot gases are cooled to 500°C in the heat exchanger, where steam is produced, before they are emitted through the stack of the power plant. Calculate the flux of mass of methane and air necessary to operate the cycle. Calculate the rates of production of entropy for the combustion and for heat transfer in the heat exchanger. (b) Let the turbine have an isentropic efficiency of 90%. Calculate the rate of entropy production in the turbine. (c) What is the rate of entropy production in the heat exchanger where the steam is condensed? (d) Express each contribution to the rate of production of entropy as a fraction of the total irreversibility.

SOLUTION: There are four sources of irreversibility to be considered (the contribution to the production of entropy in the pump is neglected). The schematic of the plant shows the corresponding four control volumes.

(a) Burning of methane with air was discussed in Example 8.11. In the accompanying diagram, the flame temperature and the rate of entropy production per mole of methane burned in unit time can be found.

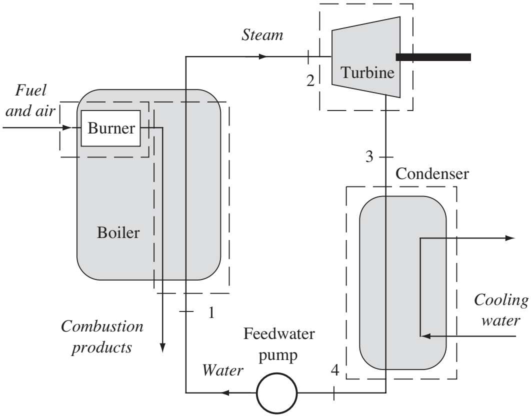

Figure Ex.13.1

The energy current $I_{E,1-2''}$ was calculated in Example 15.11 as 255 MW. Now, two expressions for the balance of energy for both the burner and the heat exchanger, and for the heat exchanger alone, can be established:

$$I_{E,1-2''} = I_n\left[\left(\bar{h}_{\text{CH4}} + 2\bar{h}_{\text{O2}} + 3.76\cdot 2h_{\text{N2}}\right)_{Ta} - \left(\bar{h}_{\text{CO2}} + 2\bar{h}_{\text{H2O}} + 3.76\cdot 2\bar{h}_{\text{N2}}\right)_{Tex}\right]$$
$$I_{E,1-2''} = I_n\left[\left(\bar{h}_{\text{CO2}} + 2\bar{h}_{\text{H2O}} + 3.76\cdot 2\bar{h}_{\text{N2}}\right)_{Tflame} - \left(\bar{h}_{\text{CO2}} + 2\bar{h}_{\text{H2O}} + 3.76\cdot 2\bar{h}_{\text{N2}}\right)_{Tex}\right]$$

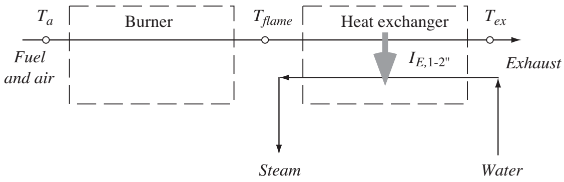

Figure Ex.13.2

I_n is the flux of amount of substance for methane, and T_{ex} denotes the temperature of the exhaust gases. T_a is set equal to 298 K. With T_{flame} = 2330 K and T_{ex} = 773 K, the flux of amount of substance of methane turns out to be 400 mole/s, which translates into a mass flux of 6.4 kg/s for methane and 110 kg/s for air. Now, with the results of Example 8.11, the rate of production of entropy in the burner must be equal to

$$\Pi_S = 763\frac{\text{W}}{\text{K}\cdot\left(\text{mole}\cdot\text{s}^{-1}\right)}\cdot 400\frac{\text{mole}}{\text{s}} = 3.05\cdot 10^5\,\text{W}/\text{K}$$

The balance of entropy for the heat exchanger, on the other hand, takes the form

$$\begin{aligned}\Pi_S &= I_{m,steam}\left(s_{2''} - s_1\right)\\ &\quad - I_{n,\mathrm{CH4}}\left[\left(\bar{s}_{\mathrm{CO2}} + 2\bar{s}_{\mathrm{H2O}} + 3.76\cdot 2\bar{s}_{\mathrm{N2}}\right)_{Tflame} - \left(\bar{s}_{\mathrm{CO2}} + 2\bar{s}_{\mathrm{H2O}} + 3.76\cdot 2\bar{s}_{\mathrm{N2}}\right)_{Tex}\right]\end{aligned}$$

or

$$\begin{aligned}\Pi_S &= 100\frac{\mathrm{kg}}{\mathrm{s}}\left(5700 - 700\right)\frac{\mathrm{J}}{\mathrm{K}\cdot\mathrm{kg}} - 400\frac{\mathrm{mole}}{\mathrm{s}}\left(2.80\cdot 10^3 - 2.35\cdot 10^3\right)\frac{\mathrm{J}}{\mathrm{K}\cdot\mathrm{mole}}\\ &= 3.20\cdot 10^5\,\mathrm{W/K}\end{aligned}$$

(b) The rate of entropy production in the turbine can be calculated according to the results of Example 15.12. The numbers computed in Example 15.11 tell us that the isentropic power of the turbine is 256MW – 162 MW = 94 MW. Therefore, the rate of entropy production is

$$\Pi_S = \frac{1}{T_L}\left(1 - \eta_{turbine}\right)I_{E,2''-3'} = \frac{1}{323}\left(1 - 0.90\right)\cdot 94\cdot 10^6\,\mathrm{W/K} = 0.29\cdot 10^5\,\mathrm{W/K}$$

(c) We have to recalculate the specific entropy of the steam leaving the turbine and entering the condenser. This is done simply by adding the entropy produced in the turbine to the value at point 2 in the power plant. With $s_3 = s_{3'} + 0.29\ \mathrm{kJ/(K\cdot kg)} = 6.0\ \mathrm{J/(K\cdot kg)}$, the balance of entropy for the condenser is given by

$$\begin{aligned}\Pi_S &= -I_{m,steam}\left(s_3 - s_1\right) + I_{m,cooling}c_{P,water}\ln\left(\frac{T_{c,out}}{T_{c,in}}\right)\\ &= -100\cdot\left(6000 - 700\right)\mathrm{W/K} + 2720\cdot 4200\cdot\ln\left(\frac{308}{293}\right)\mathrm{W/K} = 0.40\cdot 10^5\,\mathrm{W/K}\end{aligned}$$

The mass flux of the cooling water has to be recalculated as well; its new value is 2720 kg/s.

(d) Relative contributions to irreversibility and fluxes of entropy with respect to the entire plant appear in Table 15.5.

Table 15.5: Irreversibilities in a power plant

Contribution	Fraction of total
Entropy production as a result of combustion	0.44
Entropy production in boiler heat exchanger	0.46
Entropy production in turbine	0.04
Entropy production in condenser heat exchanger	0.06
Entropy flux with fuel and exhaust	0.18
Entropy flux to environment through condenser	0.82

EXERCISES AND PROBLEMS

1. Prove that the density of moist air is always smaller than that of dry air at the same temperature and pressure.
2. During the day, at a temperature of 30°C, the relative humidity of the air was measured to be 60%. How far does the temperature have to drop at night for dew to form on the grass?
3. Show that the humidity ratio given in terms of the wet bulb temperature by Equ.(15.33) can

be approximated as follows:

$$(\omega' - \omega_1)\Delta h_v = c_{Pa}(T_a - T_{wb})$$
$$\omega' = 0.622\, P_g(T_{wb})/P$$

What approximations have to be made? Give an interpretation of the first of these equations.

4. Show that the expression for the total flux of water vapor in a column of (still) humid air above a body of water is given by Equ.(15.40).
5. Derive the differential equation for diffusion of water vapor in a container as in Fig. 15.19, and show that its solution is given by Equ.(15.43).
6. A stainless steel temperature probe is placed in water and then removed with a drop of water hanging from its end. Data can be found in Equ.(6.8). Create a simple system dynamics model that might explain this phenomenon. What parameters need to be known if we wish to use the model to determine the current of water from the drop due to evaporation?
7. The Rankine-Process is a model for the processes undergone by the working fluid (water and steam) in a power plant with a steam turbine (solid line in the diagram). From 1 to 2, the water is warmed by heating. At the same time, the pressure is raised to 60 bar. Further heating leads to total evaporation (2 to 3). Then, at constant pressure, the steam is further heated (3 to 4). Between 4 and 5, the steam is expanded isentropically in the turbine (the pressure here reduces to 1 bar. Then the steam is condensed in a cooler (5 until 1). In the following, consider 1 kg of water.

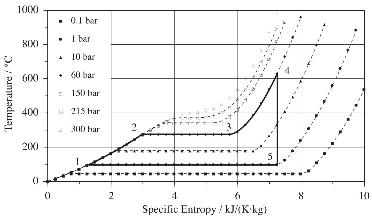

Figure P.7

(a) Treat the steam from point 3 to 4 as an ideal gas with a temperature coefficient of enthalpy (specific heat at constant pressure) of 3000 J/(K · kg). How much entropy must be introduced to the gas so that its temperature increases as seen in the diagram? Compare your theoretical calculation with the diagram. (b) How much energy is released in the cooler into the environment per kilogram of water? (The process from point 5 to 1). What is the flow of energy to the environment when the mass flow of the working fluids through the plant is 800 kg/s?

8. Determine the vapor pressure of Refrigerant 123 (R123) as a function of temperature. It is known that at 0°C the vapor pressure is 32.7 kPa. Use data from Fig. 15.24 and compare your result to Fig. P.8.

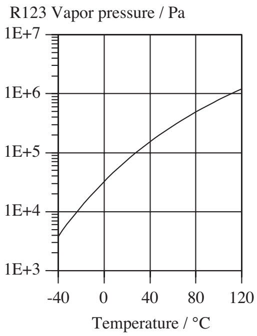

Figure P.8

9. Express the efficiency of the ideal Rankine cycle in terms of the average temperature of heating. Neglect the feed-water pump.
10. Discuss the effect of changing the upper and the lower operating pressures of the Rankine cycle. Why is a condenser used in vapor power plants if steam leaving the turbine could be discharged directly to the environment?
11. Calculate the Carnot efficiency of the cycles running between the upper and the lower operating temperatures occurring in the processes of Example 15.11 (300°C and 40°C, without superheating). Does the difference between the Carnot efficiencies and the values calculated in that example result from dissipation?

12. Assume the furnace of the Carnot cycle proposed in Problem 11 to operate at 500°C and the condenser at 20°C, respectively. The cycle undergone by the working fluid is supposed to be the same as before. Calculate the rate of production of entropy and the rate of loss of availability.
13. (a) Estimate the efficiency of a vapor power cycle without superheating designed for the fluid R123. The heat is supposed to be delivered by solar collectors such as vacuum tubes. Saturated liquid enters the evaporator at a pressure of 8.0 bar, while the condenser operates at a temperature of 30°C. (Use property data found in Fig. 15.24 and Fig. P.8.) (b) If the collectors deliver an energy current of 350 W per square meter of collector area, what is the minimum collector area needed per kW of power of the engine?
14. Estimate the amount of entropy produced in the throttling process of a refrigerant if the following data are given: the initial and the final pressure, and the initial and the final specific volume of the fluid.
15. Superheated water vapor at a pressure of 30 bar and a temperature of 300°C expands isentropically to a state with a temperature of 100°C. (Such a change might occur for adiabatic expansion of an ideal fluid in a turbine.) (a) Calculate the specific entropy and enthalpy of the fluid. (b) Determine the pressure and the temperature at which the fluid begins to condense. (c) Calculate the pressure and the quality of the fluid mixture at the final state. Perform the calculations by interpolation of the graphs provided above.
16. Superheated water vapor at a pressure of 10 bar and a temperature of 400°C is expanded in an isobaric process until the state of saturated liquid is reached. (a) How much entropy must be emitted or absorbed by 10 kg of the fluid? (b) How much energy is transferred in heating or in cooling? (c) How much energy has been transferred as a consequence of the mechanical process? Use tables provided in this chapter for calculations.

CHAPTER 16

SOLAR RADIATION

In this final chapter, solar radiation and aspects of its nature that are important in solar energy engineering will be discussed. The results concerning radiative transfer of entropy and energy, and spectral distributions of radiation derived in Chapter 12 will be made use of.

16.1 SOLAR RADIATION

Our Sun is a rather average main sequence star[1] of spectral type G2[2] which means that it has a surface temperature of a little less than 6000 K and pours out radiation with an energy flux of $4 \cdot 10^{26}$ W. At the distance of the Earth, this flux has thinned out to a flux density (normal irradiance) of 1360 W/m^2. This is the radiation which penetrates the Earth's atmosphere, sets in motion many of the processes in the air and in the oceans, and makes possible the existence of life.

In the last section of this chapter, we will consider the origin and the form of solar radiation found outside our atmosphere, before discussing radiative processes in the atmosphere. This should lead to an assessment of the entropy and the temperature of the radiation found at the surface of the Earth including a process which was left out of consideration so far, namely, scattering of radiation. Finally, two subjects of interest in solar energy engineering will be addressed: the concentration of sunlight to achieve high temperatures, and the absorption of radiation by simple flat solar collectors.

16.1.1 The Origin of Solar Radiation

Stars such as our Sun are spheres made of hydrogen and helium (plus a small fraction of the heavier elements), which under the influence of their own gravity attain high

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[1] Main sequence stars are those in the first and longest phase of their life, during which they burn hydrogen at their centers. On astrophysics in general, see F. H. Shu (1982); on stars in particular, see C. Payne-Gaposhkin (1979), or I.S. Shklovskii (1978).

[2] The spectra of normal stars are put into a sequence representing decreasing surface temperature which corresponds to changing the apparent color of the star from blue to red. The sequence is labeled O B A F G K M, and it represents surface temperatures from some 20000 K to about 3000 K.

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_17,

pressures and temperatures at their centers that allow nuclear reactions to occur. It is believed that all the energy released as a consequence of these reactions is carried outward and radiated away from the surface. Since solar material is fairly opaque, the radiation we receive essentially originates in a thin layer at the surface of the star. This radiation then spreads through space, a process which preserves the essential characteristics of the light, namely, its entropy and energy intensity and, therefore, its temperature.

The interior of the Sun. Our central star is a sphere of gas with a radius of about 696,000 km and a mass of $1.989 \cdot 10^{30}$ kg, made out of hydrogen (70% by mass), helium (27%), and a sprinkling of heavier elements (3%).[3] The composition of stars is derived from spectral observations of their surfaces. Naturally, to take this as the composition of the interior as well, we must have reason to believe that a star is well mixed. Indeed, it is assumed that during formation the material of a star is subject to heavy mixing, leading to a uniform composition. Now, since few stars, including our Sun, are found to be precisely at the beginning of their life, we can assume that the changes of composition due to nuclear reactions in the interior do not reach the surface. Models of the structure of main sequence stars show that convection occurs in these objects either deep inside the core, or near the outer layers only, which prevents mixing of the interior and the surface.

Therefore, new stars can be considered to be uniform spheres of gas. For a given composition, there is essentially only one parameter which distinguishes between different stars and influences their evolution from newly born to old and highly evolved—the mass of the object. Masses of stars span a range of about one hundredth of the mass of our Sun to maybe 100 times its mass. Since during their first stage of evolution as main sequence stars changes occur rather gradually, one is justified in approximating their structure as spherically symmetric fluid bodies in hydrostatic equilibrium. A simple calculation[4] shows that the pressure at the center of a sphere with the properties of our Sun should be around $6 \cdot 10^{14}$ Pa. Assuming ideal gas properties we then estimate the central temperature of the Sun to be some 10 million K. This result justifies the initial assumption that the matter inside a star must behave very much like an ideal gas[5] even at densities of 100 times that of water, a value which comes close to that at the center of the Sun. The temperatures found at and near the center of a star are high enough to allow for hydrogen burning to occur (hydrogen fuses into helium). These nuclear reactions release the vast amounts of energy which, in the end, are carried away with the radiation from the surface of the star. Before this can happen, however, entropy and energy need to be transported from the interior to the surface.

It is found that, again for properties encountered in main sequence stars, conduction of heat is negligible. This leaves convection and radiation as modes of transfer. If the temperature gradient required for the diffusion of radiation (see Section 12.2.5) is not too large, radiation will prevail and the gas inside the star will be stable against convective disturbances (Section 14.4). If, on the other hand, the temperature gradient re-

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[3] Numbers can be found in K.R. Lang (1980).

[4] Consider a column of fluid extending from the center to the surface and calculate its weight from an average value of the gravitational field inside the star. See Schwarzschild (1958) for a simple discussion of the interior state of stars.

[5] The atoms inside a star must be completely ionized, leading to a gas made out of nuclei and electrons, both behaving as ideal gases for the states found inside main sequence stars.

quired for transporting all the heat becomes too large, convection will set in and totally dominate the transport mechanisms. Now, numerical models of the interior of well mixed spheres of gas show that stars of solar mass are stable against convection in their inner parts. Further out toward the surface, however, radiation can no longer carry the fluxes of entropy and energy; convection starts and takes over the transport all the way to the surface. With stars whose mass is larger than about twice that of the sun the interior state is just the opposite. Because of the much higher rate of release of energy at the center compared to solar-type stars, convection is required for the inner parts while radiation occurs in the outer layers.

Changes of the initial structure of stars are essentially a consequence of nuclear reactions near the center which slowly change the composition of the gas.[6] As a result, the interior structure changes considerably. It is interesting to see that during the hydrogen burning phase, the exterior appearance of the main sequence stars does not change nearly as much.

Radiation from the surface of stars. Models calculated on the basis of the processes just described yield the radius and the luminosity of the star in addition to details on the interior state.[7] These values allow for the temperature of the surface of the star to be calculated if we assume the radiation to be that of a black body (Fig. 12.10). As we know from the laws of hemispherical emission from the surface of a black body, the relation between hemispherical flux, surface area, and temperature yields

$$L = 4\pi R_s^2 \sigma T_s^4 \tag{16.1}$$

In astronomy, the energy flux carried away from the surface of a star is called the luminosity L. Currently, the luminosity of the Sun, as measured from the radiation above the Earth's atmosphere,[8] is $3.844 \cdot 10^{26}$ W. With a radius of $6.96 \cdot 10^{8}$ m, the equivalent blackbody temperature for the surface of the Sun is 5777 K. If we do this calculation for the one-parameter sequence of models of gas spheres for varying mass, we may plot the result in a luminosity-temperature diagram which is called the Hertzsprung-Russell diagram (Fig. 16.1). The most interesting result of these computations shows that the surface properties put the model stars along a line from the upper left to the lower right in the diagram precisely where observations place the so-called main sequence stars. Therefore, main sequence stars are interpreted as stars in the first phase of their life, during which they transform hydrogen into helium. They stay in a narrow band along the main sequence in the Hertzsprung-Russell diagram as long as they have enough hydrogen at the center for this type of nuclear reaction to occur.

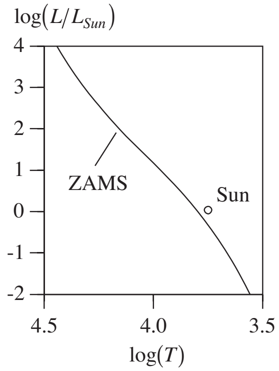

Figure 16.1: Hertzsprung-Russell diagram of main sequence stars. The diagram shows the logarithm of the ratio of the luminosity of a star to that of the sun as a function of the logarithm of the surface temperature. The result holds for models of zero age main sequence (ZAMS) stars. Results of model calculations have been taken from Iben (1967).

The radiation field at the surface of the sun and at the distance of the Earth. As you can see by comparing the measured spectrum of solar radiation with that of a black body of equivalent temperature (Fig. 16.2), for the purpose of solar energy engineering solar radiation quite nicely approximates the ideal case.

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6. Stars of solar mass have a luminosity which allows them to burn hydrogen at their centers for some 10 billion years. A star of 5 solar masses, however, burns so fast that hydrogen will be depleted in the inner regions in about 70 million years.
7. See D.D. Clayton (1968) for an account of stellar structure and evolution.
8. The value of the luminosity of the Sun is the result of the integration of the WRC spectrum over wavelength (Figures 12.8 and 16.2).

The radiation emitted by our Sun originates in the uppermost layers at the surface. This part of the Sun is called the photosphere; obviously, conditions there are more complicated than envisioned by the model of a black body. What you cannot see in the spectrum in Fig. 16.2 are the many narrow absorption lines which result from atomic absorption in the outermost layers of the photosphere. These lines provide most of the detailed information about the conditions at the surface of our star. In particular, through spectroscopy we determine the composition of the Sun's surface. In the last century, a new element was found in the solar spectrum in this way which received the name of the Sun, helium.

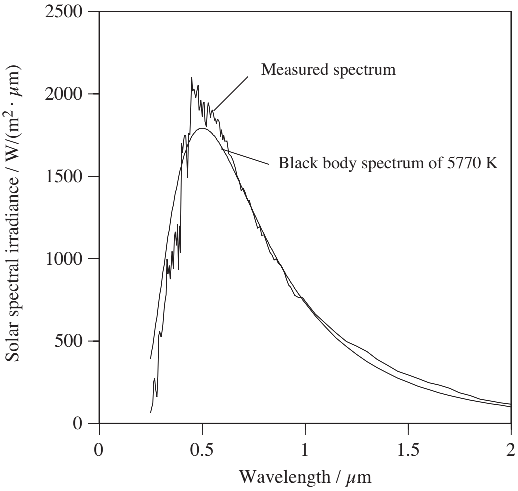


Figure 16.2: Black body spectrum for a temperature of 5770 K superimposed on the spectrum of solar radiation observed above the surface of the Earth's atmosphere. Since the properties of the radiation do not change on their way from the Sun to the Earth, the spectrum is equal to that found at the surface of the Sun, multiplied by the (constant) solid angle of the Sun as seen from the Earth.

Following the discussion of the laws for monochromatic radiation in Section 12.3, we may derive the values of the entropy intensity and the temperature for different wavelengths for the radiation at the surface of the Sun. According to Equations (12.50) and (12.35), and Problem 7 of Chapter 12, the entropy intensity is given by

$$i_{s\lambda} = \frac{2kc}{\lambda^4}\left\{\left(1+\frac{\lambda^5 i_{E\lambda}}{2hc^2}\right)\ln\left(1+\frac{\lambda^5 i_{E\lambda}}{2hc^2}\right)-\frac{\lambda^5 i_{E\lambda}}{2hc^2}\ln\frac{\lambda^5 i_{E\lambda}}{2hc^2}\right\} \tag{16.2}$$

while the monochromatic temperature is computed from Equ.(12.52) which yields

$$T_\lambda = \frac{hc}{k\lambda}\frac{1}{\ln\left(\dfrac{2hc^2}{\lambda^5 i_{E\lambda}}+1\right)} \tag{16.3}$$

Calculation of the monochromatic temperature and the entropy intensity for both the measured values of the solar spectrum and its equivalent blackbody spectrum shows (Fig. 16.3) that the difference between the actual radiation and the ideal one is small. Integration of the spectral entropy intensity yields a value which is only slightly larger for the blackbody spectrum than for the actual one. (Since turning solar radiation into an equivalent blackbody spectrum should produce entropy, this result is to be expected.) Especially in the range where the Earth's atmosphere lets most of the radiation pass, the deviation is very small. We should expect changes in the radiation from blackbody conditions to result mostly from the interaction with our atmosphere.

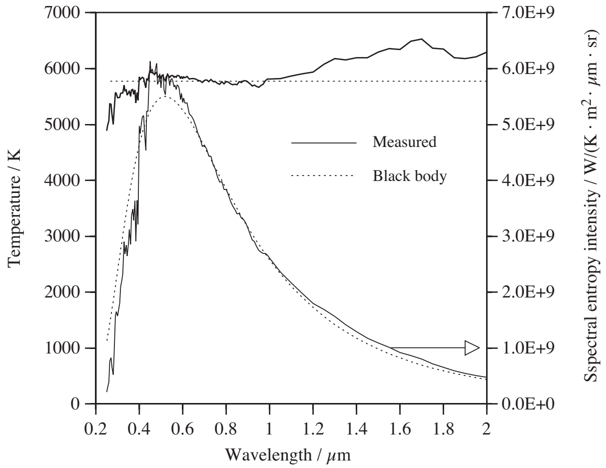


Figure 16.3: Monochromatic temperature of the radiation from the surface of the sun both for measured values and for a blackbody spectrum at 5777 K. Also shown are the entropy intensities for measured values and for the equivalent blackbody spectrum.

16.1.2 Absorption, Scattering, and Polarization in the Atmosphere

The Earth's atmosphere changes the physical state of solar radiation arriving at the surface of our planet considerably (Fig. 16.4). Different molecules absorb some of the light, and molecules and aerosols scatter part of it. As a result, for cloudless skies, we have both direct and diffuse radiation, where the diffuse part is composed of the light which has been scattered. There is still another effect which should be taken into account: scattering polarizes the rays that are essentially unpolarized before they hit the atmosphere.

Naturally, the magnitude of the effects depends both upon the properties of the atmosphere and its thickness, i.e., the amount of air solar rays must penetrate (Fig. 16.4). The latter quantity is called relative *air mass*, where an air mass equal to 1 means that the sun is precisely overhead. If we give the position of the sun in the sky in terms of its zenith angle θ, we can calculate the distance solar rays have to travel through the atmosphere to the observer. For angles not too close to 90°, the relative air mass m_a is

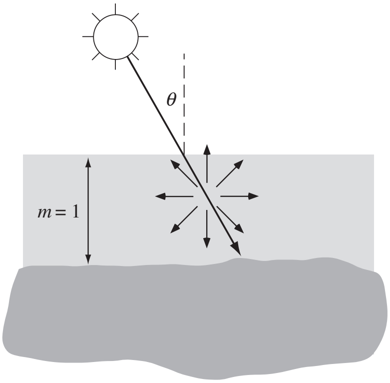
$$m_a(\theta) = \frac{1}{\cos(\theta)} \qquad \textbf{(16.4)}$$

Note that the solar irradiance for the horizontal surface at the top of the atmosphere depends upon the zenith angle of the Sun as well:

$$\mathcal{G}_{ho} = \cos(\theta)\mathcal{G}_{sc} \qquad \textbf{(16.5)}$$

where $\mathcal{G}_{sc}$ is the solar constant of 1367 W/m², which is obtained from integration of the WRC spectrum (Fig. 16.2). The following points will be discussed for a cloudless atmosphere only.

Figure 16.4: When solar radiation penetrates the Earth's atmosphere, it is both absorbed and scattered. In addition, while extraterrestrial radiation is more or less unpolarized, scattering polarizes the light arriving at the surface of the planet. All these effects change the relative amounts of entropy and energy of radiation, therefore leading to changes of the monochromatic temperatures.



Attenuation of solar radiation. The influence of the Earth's atmosphere is commonly described in terms of *attenuation or extinction coefficients* which should be given for every wavelength. An extinction coefficient is the sum of absorption coefficient and scattering coefficient, i.e.,

$$\mu_\lambda = \kappa_{E\lambda} + \beta_{E\lambda} \tag{16.6}$$

(see Problem 5 in Chapter 12), and it is defined so that

$$\frac{di_{E\lambda}(s)}{ds} = -\mu i_{E\lambda}(s) \tag{16.7}$$

which, for constant attenuation coefficients along a path *s* turns out to be equivalent to

$$i_{E\lambda}(s) = i_{E\lambda o} \exp(-\mu s) \tag{16.8}$$

In these equations, *s* is the length of the path travelled by a ray in the atmosphere, and the index *o* refers to the radiation above the atmosphere. In solar radiation computations, it is common to refer the extinction coefficients to relative air mass, which means that you need to replace *s* by m_a, according to Equ.(16.4), in the equations. Since the term containing the exponential function gives the ratio of the transmitted light to the incident light, it is called the *transmittance* τ of the atmosphere:

$$\tau_\lambda = \exp(-k_\lambda m_a) \tag{16.9}$$

where k_λ replaces the normal extinction coefficient. If the coefficients and the original undisturbed spectrum are known, the effect of the atmosphere can be computed for every wavelength upon which the total influence is obtained by integration over the spectrum.

Absorption and scattering. Absorption of a ray of light by a clear atmosphere is due to molecular effects, and strongly depends upon wavelength, leading to absorption bands in the solar spectrum at the surface of the Earth. In the part of the radiation extending from short wavelengths up to 0.35 µm, the most important contribution to molecular absorption comes from ozone; absorption bands due to water vapor influence the radiation mostly between 1 µm and 4 µm; and the uniformly mixed gases mainly absorb at wavelengths above 2 µm. Aerosols add a little bit to absorption but their main influence is upon scattering and will be considered later (Fig. 16.5).[9]

The spectral transmittance of ozone is calculated in terms of the attenuation coefficient $k_{O\lambda}$, the amount of ozone, which is given as an equivalent length l in cm, and the air mass m_a:[10]

$$\tau_{O\lambda} = \exp\left(-k_{O\lambda} l m_a\right) \tag{16.10}$$

The attenuation coefficient has been measured and is given in tables. For uniformly mixed molecular absorbers such as CO_2 and O_2, the combined effect is

$$\tau_{g\lambda} = \exp\left(-\frac{1.41 k_{g\lambda} m_a}{\left(1 + 118.93 k_{g\lambda} m_a\right)^{0.45}}\right) \tag{16.11}$$

while water vapor absorption is calculated according to

$$\tau_{wa\lambda} = \exp\left(-\frac{0.2385 k_{wa\lambda} w m_a}{\left(1 + 20.07 k_{wa\lambda} w m_a\right)^{0.45}}\right) \tag{16.12}$$

where w is the amount of precipitable water given in cm.[11] Note that the form of these laws for the transmittance differ somewhat from the simple form presented above in Equ.(16.9); they are the result of parameterization of more detailed absorption calculations.

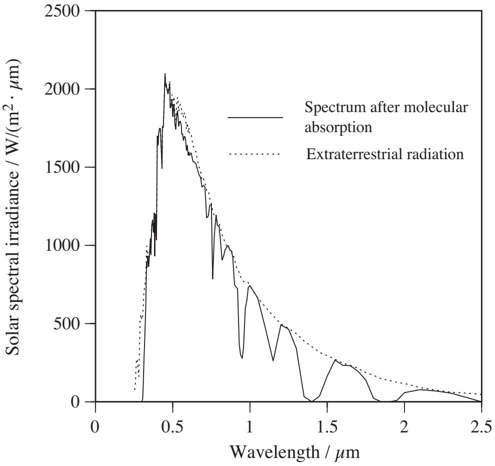


Figure 16.5: Molecular absorption changes the extraterrestrial radiation in some areas of the spectrum. If scattering is neglected, the radiation changes according to the data shown in this graph. The amount of ozone used in the calculation corresponds to 0.35 cm, and that for water vapor to 2 cm, while the air mass was taken to be 2. Spectral absorption coefficients have been taken from Iqbal (1983, Tables 6.12.1, 6.13.1, 6,13.2, and Appendix C therein).

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[9] The discussion in this section is based upon Iqbal (1983), Chapter 6.

[10] We should use the relative air mass for ozone which differs from the normal value for large zenith angles of the Sun (Iqbal, 1983, Chapter 5).

[11] See Iqbal (1983), Chapter 5.4.

Let us now turn to a brief description of scattering. Light traveling along a beam through the atmosphere is partly absorbed and partly scattered; only the contribution which is not influenced by either mechanism is transmitted to the ground. Scattering removes radiation from a beam by changing the direction of incoming radiation; the frequency and energy of the scattered component are not changed, but the change of directional distribution certainly leads to changes in the intensity of the light. The latter process has important consequences for the entropy and the temperature of scattered radiation (see below); scattering is an irreversible process.

There are two distinct effects to be taken into account, namely scattering from molecules (*Rayleigh scattering*) and from larger particles (*Mie scattering*). The distribution of the directions of scattered radiation is not generally isotropic. While in Rayleigh scattering equal amounts are scattered in forward and backward directions, forward scattering is preferred in Mie scattering. There is a clear difference between scattering and absorption in that the former is a continuum effect while the latter is selective with respect to wavelength.

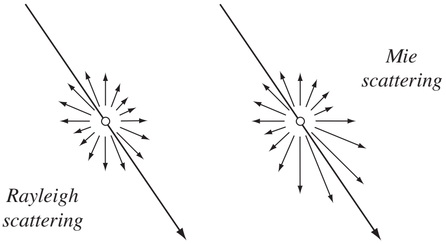

Figure 16.6: Scattering of a ray of light leads to a redistribution of directions of radiation without changing the energy and the frequency. In Rayleigh scattering, forward and backward scattering are favored equally over sideways scattering. In Mie scattering, due to larger particles, forward scattering is dominant.

Both effects are described in terms of the part of the incident ray which is transmitted without being scattered. In the case of Rayleigh scattering, the transmittance is calculated as follows:

$$\tau_{r\lambda} = \exp\left(-\frac{8.735 \cdot 10^{-3} m_a}{\lambda^{4.08}}\right) \tag{16.13}$$

Note that in this and the following formula, the wavelength must be given in µm. Mie scattering may be expressed in terms of two factors α and β which describe the turbidity of the atmosphere:[12]

$$\tau_{a\lambda} = \exp\left(-\frac{\beta m_a}{\lambda^{\alpha}}\right) \tag{16.14}$$

The factor β varies from 0 to 0.4 for clean to very turbid atmosphere (visibility ranging from 340 km to less than 5 km), while α is around 1.3.

Note that scattering strongly depends upon the frequency of light, short wavelengths being preferred. Rayleigh scattering in particular leads to the filtering out of blue light from a beam. The transmittance due to this effect is zero at 0.3 µm, while at 0.6 µm it is already above 90%; this explains the blue color of the sky.

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[12] Angström's turbidity formula for aerosols; see Iqbal (1983), p. 117–119.

Calculation of direct and diffuse radiation upon the ground. The formulae presented for absorption and for scattering now allow us to calculate the solar radiation expected at the ground for the case of cloudless atmospheres. The direct ray is attenuated as a result of both absorption and scattering, which means that the part transmitted can be calculated from the radiation incident upon the atmosphere and the product of all transmittances:

$$\mathcal{G}_{\lambda hb} = \tau_{r\lambda}\tau_{a\lambda}\tau_{g\lambda}\tau_{O\lambda}\tau_{wa\lambda}\cos(\theta)\mathcal{G}_{\lambda o} \tag{16.15}$$

Here, $\mathcal{G}_{\lambda o}$ is the spectral irradiance at the top of the atmosphere, measured for a surface normal to the rays, while $\mathcal{G}_{\lambda hb}$ represents the transmitted spectral direct (beam) irradiance for a horizontal surface. The amount of radiation scattered is then calculated according to

$$\mathcal{G}_{\lambda hs} = \tau_{g\lambda}\tau_{O\lambda}\tau_{wa\lambda}\left(1-\tau_{r\lambda}\tau_{a\lambda}\right)\cos(\theta)\mathcal{G}_{\lambda o} \tag{16.16}$$

where s stands for scattered. There is a problem with calculating the diffuse radiation reaching the ground from the total amount scattered unevenly in all directions. The simplest possibility, which still neglects the effect of light reflected from the ground and scattered back by the atmosphere, is to assume that exactly half of the originally scattered radiation flows downward from the sky to the ground. (This is the assumption made in the calculations which led to the results presented in Fig. 16.7.) The sum of the direct and the diffuse radiation is called global radiation.

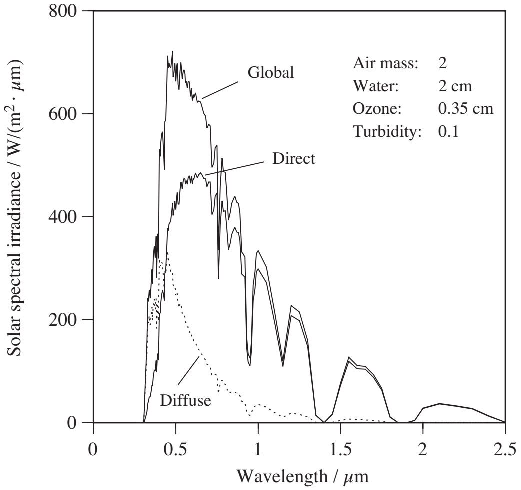

Figure 16.7: Computed spectral distribution of direct and diffuse solar radiation for the horizontal surface for a cloudless sky. It is assumed that precisely half of all the radiation scattered flows in the direction of the ground. The sum of direct and diffuse irradiance is called *global* irradiance. The computation starts with the WRC spectrum and assumes absorption and scattering according to the relations presented in this section. Values of absorption coefficients have been taken from Iqbal (1983). See also Fig. 16.5.

The entropy and the temperature of solar radiation. According to Planck's theory presented in Section 12.3, we can associate a spectral entropy intensity and a monochromatic temperature with radiation of a given spectral energy intensity. To find the entropy and the temperature according to Equations (16.2) and (16.3) we have to calculate the energy intensity for direct and diffuse radiation from Equations (16.15) and (16.16), respectively. For the former we obtain

$$i_{E\lambda b} = \frac{1}{\cos(\theta)} \frac{\mathcal{G}_{\lambda hd}}{\Omega_s} \tag{16.17}$$

where Ω_s is the solid angle of the Sun as seen from the Earth, which is equal to

$$\begin{aligned}\Omega_s &= \frac{\pi R_S^2}{d_{ES}^2} \\ &= \frac{\pi\left(6.960 \cdot 10^8\right)^2}{\left(1.496 \cdot 10^{11}\right)^2} = 6.80 \cdot 10^{-5}\,\mathrm{sr}\end{aligned}$$

The cosine of the zenith angle of the Sun appears in Equ.(16.17) since we have to take a surface normal to the direction of the direct beam. For the diffuse component of solar radiation, on the other hand, we take the light scattered to the horizontal surface. If we assume half of the radiation scattered in all directions to reach the ground, and if we take this component to have an isotropic distribution over the hemisphere, the energy intensity is given by

$$i_{E\lambda d} = \frac{0.5\mathcal{G}_{\lambda hs}}{\pi} \tag{16.18}$$

This follows from Equ.(12.13) for isotropic hemispherical radiation. The values obtained from Equations (16.17) and (16.18) are plugged into the relations for the entropy intensity and the monochromatic temperature. The temperature of solar radiation is presented in Fig. 16.8 for the spectrum shown in Fig. 16.7.

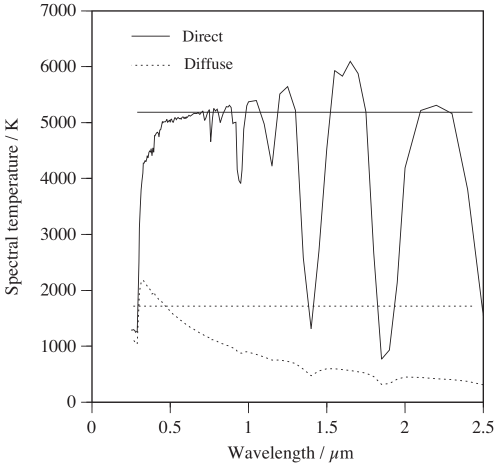

Figure 16.8: Spectral temperatures of direct and diffuse radiation according to the spectra given in Fig. 16.7. The horizontal lines represent effective temperatures of overall radiation calculated according to Equation (216). For visible light, the temperature of direct radiation is close to 5100 K while that for diffuse light is between 1500 K and 2000 K.

Obviously, absorption and scattering will change black radiation into nonblack light. Both effects reduce and redistribute the spectral intensities leading to a spectrum of temperatures for radiation which originally had only a single temperature. We may introduce the "effective" temperature of a component of radiation by comparing the integral values of entropy and energy intensity. According to Equ.(12.5) and its counterpart for energy we may write

$$i_E = \frac{3}{4} T_{eff} i_S \tag{16.19}$$

This quantity is shown in Fig. 16.8 for both direct and diffuse solar radiation. Calculations show that the effective temperature of direct light is only slightly smaller than the temperature of the surface of the Sun, even for relatively low elevation of the Sun in the sky. (For the spectrum calculated in Fig. 16.7 the value turns out to be roughly 5100 K.) The temperature of diffuse light from the sky still has a surprisingly high temperature of around 1700 K. Detailed studies of the entropy of solar radiation[13] demonstrate that the main assumption made here with regard to diffuse light, namely, that it is supposed to be isotropic, is acceptable. Assuming realistic angular distributions leads to changes in the results of only a few percent.

Polarization of solar radiation. There is another effect which could be of interest because of its influence upon the entropy and the temperature of radiation, namely polarization. For the case of solar radiation in the Earth's atmosphere we need models of the degree of polarization as a function of the angles of incidence of diffuse light (scattered and reflected). Again, for realistic models of solar radiation, the effect of polarization upon the temperature of radiation is relatively minor. Allowing for complete polarization, however, reduces the entropy of radiation by about 20% compared to the value for unpolarized light.[13]

QUESTIONS

1. How can the radiant power of the Sun be obtained from measurements of the solar constant? Assuming that the energy current from the surface of the Sun has been obtained, how can we infer the Sun's surface temperature?
2. Consider a main sequence star having 1000 times the luminosity of the Sun (Fig. 16.1). How do you find its radius?
3. Are the values of the Sun's radiation shown in Fig. 16.2 for the surface of the Sun or for its radiation above the Earth's atmosphere?
4. What is the meaning of air mass 1?
5. What is the condition of validity of Equ.(16.9)?
6. How does knowledge of the entropy and the energy of radiation yield its temperature?
7. If we wish to make use of solar radiation for engineering applications (such as in solar thermal or photovoltaic systems), what is the importance of knowing the temperature of the direct and diffuse components of radiation? (See Fig. 16.8.)

EXAMPLE 16.1. Calculating direct and diffuse spectral irradiances.

Calculate the spectral irradiances of direct and diffuse sunlight for a wavelength of 600 nm for the following atmospheric conditions. The solar elevation is taken to be 30°. The amount of ozone and of water vapor are set to 0.35 cm and 2.0 cm, respectively. The Angstöm coefficients for the turbid atmosphere are set equal to $\beta = 0.10$ and $\alpha = 1.3$, respectively.

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[13] Kabelac and Drake, 1992, p. 239–246.

SOLUTION: According to Iqbal (1983), the values of the extraterrestrial spectral irradiation and the molecular absorption coefficients are given by

λ / µm	G_λ / W/m^{2}µm	$k_{O\lambda}$	$k_{g\lambda}$	$k_{wa\lambda}$
0.600	1720.00	0.125	0.00E+00	0.00E+00

We have to calculate the transmission coefficients due to absorption and to scattering according to Equations (16.10) through (16.14). Since the absorption coefficients for the uniformly mixed gases and for water vapor are equal to zero at the chosen wavelength, we only have to take into account Equ.(16.10) for absorption by ozone:

$$\tau_{O\lambda} = \exp\left(-k_{O\lambda} l m_a\right) = \exp\left(-0.125\cdot 0.35\cdot 2\right) = 0.916$$

Since the elevation of the Sun is 30°, the zenith angle is 60° which yields a value for the relative air mass of 2.0. Scattering leads to following two transmittances:

$$\begin{aligned}\tau_{r\lambda} &= \exp\left(-8.735\cdot 10^{-3} m_a / \lambda^{4.08}\right) = \exp\left(-8.735\cdot 10^{-3}\cdot 2/0.600^{4.08}\right) = 0.869\\ \tau_{a\lambda} &= \exp\left(-\beta\cdot m_a/\lambda^{\alpha}\right) = \exp\left(-0.1\cdot 2/0.600^{1.3}\right) = 0.678\end{aligned}$$

All in all, the direct spectral irradiance on the horizontal must be

$$\begin{aligned}\mathcal{G}_{\lambda hb} &= \tau_{r\lambda}\tau_{a\lambda}\tau_{g\lambda}\tau_{O\lambda}\tau_{wa\lambda}\cos(\theta)\,\mathcal{G}_{\lambda o}\\ &= 0.869\cdot 0.678\cdot 1\cdot 0.916\cdot 1\cdot 0.5\cdot 1720\,\mathrm{W}\big/\left(\mathrm{m}^2\mu\mathrm{m}\right) = 464\,\mathrm{W}\big/\left(\mathrm{m}^2\mu\mathrm{m}\right)\end{aligned}$$

The diffuse radiation, on the other hand, is

$$\begin{aligned}\mathcal{G}_{\lambda hs} &= 0.5\cdot\tau_{g\lambda}\tau_{O\lambda}\tau_{wa\lambda}\left(1-\tau_{r\lambda}\tau_{a\lambda}\right)\cos(\theta)\,\mathcal{G}_{\lambda o}\\ &= 0.5\cdot 1\cdot 0.916\cdot 1\cdot\left(1-0.869\cdot 0.678\right)\cdot 0.5\cdot 1720\,\mathrm{W}\big/\left(\mathrm{m}^2\mu\mathrm{m}\right) = 162\,\mathrm{W}\big/\left(\mathrm{m}^2\mu\mathrm{m}\right)\end{aligned}$$

where we have assumed that half of the scattered light strikes the ground. These values can also be read from the curves in Fig. 16.7.

EXAMPLE 16.2. Entropy produced in scattering.

Consider solar radiation penetrating the Earth's atmosphere, and assume it to be undisturbed blackbody radiation of temperature 5777 K. Calculate the entropy generated if all the radiation in the wavelength band 595 – 605 nm is scattered isotropically in all directions.

SOLUTION: We first have to calculate the entropy intensity of the incident radiation for the spectral range chosen:

$$j_S = \frac{2kc}{\lambda^4}\left\{\left(1+\frac{\lambda^5 i_{E\lambda}}{2hc^2}\right)\ln\left(1+\frac{\lambda^5 i_{E\lambda}}{2hc^2}\right)-\frac{\lambda^5 i_{E\lambda}}{2hc^2}\ln\frac{\lambda^5 i_{E\lambda}}{2hc^2}\right\}\Delta\nu\,\Omega_s$$

where

$$i_{E\lambda} = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/k\lambda T}-1}$$

Plugging in values yields

$$
\begin{aligned}
i_{E\lambda} &= \frac{2\cdot 6.62\cdot 10^{-34}\cdot\left(3\cdot 10^{8}\right)^{2}}{\left(6\cdot 10^{-7}\right)^{5}\left(\exp\left(\dfrac{6.62\cdot 10^{-34}\cdot 3\cdot 10^{8}}{1.38\cdot 10^{-23}\cdot 6\cdot 10^{-7}\cdot 5777}\right)-1\right)}\\
&= 2.45\cdot 10^{13}\,\mathrm{W\,/\,(m^{2}m\cdot sr)}
\end{aligned}
$$

and

$$
\begin{aligned}
j_S &= \frac{2kc}{\lambda^4}\left\{(1+0.016)\ln(1+0.016)-0.016\ln(0.016)\right\}10\cdot 10^{-9}\cdot 6.80\cdot 10^{-5}\,\mathrm{W}\Big/\left(\mathrm{K\cdot m^2}\right)\\
&= 5.25\cdot 10^{9}\cdot 10\cdot 10^{-9}\cdot 6.80\cdot 10^{-5}\,\mathrm{W}\Big/\left(\mathrm{K\cdot m^2}\right)\\
&= 3.57\cdot 10^{-3}\,\mathrm{W}\Big/\left(\mathrm{K\cdot m^2}\right)
\end{aligned}
$$

Now, half of the irradiance is scattered into the hemisphere. The energy intensity of the scattered light is therefore

$$
i_{E\lambda,\,scatt} = \frac{\Omega_s}{\pi}0.5\cdot i_{E\lambda} = 2.65\cdot 10^{8}\,\mathrm{W}\Big/\left(\mathrm{m^2m\cdot sr}\right)
$$

The scattered entropy flux density turns out to be

$$
\begin{aligned}
j_{s,\,scatt} &= \frac{2kc}{\lambda^4}\left\{\left(1+1.73\cdot 10^{-7}\right)\ln\left(1+1.73\cdot 10^{-7}\right)-1.73\cdot 10^{-7}\ln\left(1.73\cdot 10^{-7}\right)\right\}\\
&\qquad\qquad\times 10\cdot 10^{-9}\cdot\pi\;\;\mathrm{W}\Big/\left(\mathrm{K\cdot m^2}\right)\\
&= 1.83\cdot 10^{5}\cdot 10\cdot 10^{-9}\cdot\pi\;\;\mathrm{W}\Big/\left(\mathrm{K\cdot m^2}\right)\\
&= 5.76\cdot 10^{-3}\,\mathrm{W}\Big/\left(\mathrm{K\cdot m^2}\right)
\end{aligned}
$$

Comparison with the original result shows that the rate of entropy production per square meter is $2.19\cdot 10^{-3}$ W/(K·m^2).

EXAMPLE 16.3. Monochromatic temperature of solar radiation.

Calculate the monochromatic temperature of direct and diffuse solar radiation at 600 nm for the conditions used in Example 16.1.

SOLUTION: Monochromatic temperatures are calculated according to Equ.(16.3):

$$
T_\lambda = \frac{hc}{k\lambda}\frac{1}{\ln\left(\dfrac{2hc^2}{\lambda^5 i_{E\lambda}}+1\right)}
$$

Now, the direct and the diffuse irradiances have been computed in Example 16.1. The normal direct spectral irradiance is 464 W/(m^{2}µm)/cos(60°) = $9.28\cdot 10^8$ W/(m^{2}m), while the value for the diffuse light is 162 W/(m^{2}µm) = $1.62\cdot 10^8$ W/(m^{2}m). The spectral energy intensities are therefore equal to

$$
i_{E\lambda,\,dir} = \frac{1}{\Omega_s}\mathcal{G}_{\lambda n,\,dir} = \frac{9.28\cdot 10^{8}}{6.80\cdot 10^{-5}}\mathrm{W}\Big/\left(\mathrm{m^2m\cdot sr}\right) = 1.37\cdot 10^{13}\,\mathrm{W}\Big/\left(\mathrm{m^2m\cdot sr}\right)
$$

and

$$i_{E\lambda,\,diff}=\frac{1}{\pi}\mathcal{G}_{\lambda,\,diff}=\frac{1.62\cdot 10^{8}}{\pi}\,\mathrm{W}\big/\left(\mathrm{m}^{2}\mathrm{m}\cdot\mathrm{sr}\right)=5.16\cdot 10^{7}\,\mathrm{W}\big/\left(\mathrm{m}^{2}\mathrm{m}\cdot\mathrm{sr}\right)$$

The appropriate temperatures then turn out to be

$$T_{\lambda,\,dir}=\frac{hc}{k\cdot 6\cdot 10^{-7}}\frac{1}{\ln\left(\dfrac{2hc^{2}}{\left(6\cdot 10^{-7}\right)^{5}1.37\cdot 10^{13}}+1\right)}=5072\,\mathrm{K}$$

$$T_{\lambda,\,diff}=\frac{hc}{k\cdot 6\cdot 10^{-7}}\frac{1}{\ln\left(\dfrac{2hc^{2}}{\left(6\cdot 10^{-7}\right)^{5}5.16\cdot 10^{7}}+1\right)}=1394\,\mathrm{K}$$

which can also be read off the curves displayed in Fig. 16.8. For a less turbid atmosphere and for higher elevation of the Sun, the temperature of the direct beam approaches that of the surface of the sun. Diffuse radiation has a surprisingly high temperature which might be useful in solar energy engineering.

16.2 SELECTIVE ABSORBERS

Experience shows that bodies having different surface characteristics attain different temperatures if they are exposed to the light of the Sun. Gray bodies which have the same geometrical properties should, on the other hand, all have the same temperature if placed in the same radiation field (see Example 7.12). For this reason, we should generally expect the rates of absorption and emission to depend upon the frequency of the radiation involved in the processes. The most striking case of selective absorption and emission of radiation is the greenhouse effect, which heats up the surfaces of the Earth and of Venus and the interior of glass-covered spaces well beyond levels expected from an oversimplified analysis.

16.2.1 Temperature of Absorbers Exposed to the Light of the Sun

Consider a body in sunlight. If the light is not concentrated, it will most likely attain a temperature of a few hundred Kelvin, and radiate with a spectrum bearing the mark of this hotness. On the other hand, solar radiation that is absorbed has a much higher temperature. Therefore solar radiation and radiation emitted by bodies here on Earth essentially occupy two distinct regions of the spectrum. Now consider a body with a surface having a high absorptivity for radiation at short wavelengths (solar radiation) but being a poor emitter for long wavelength radiation. The simplest model for dealing with this case is to treat the absorptivity of surfaces as having two distinct but constant values for the two separate frequency intervals of interest. Each value represents some average for radiation in each of the two sections of the spectrum (Fig. 16.9).

To find surface temperatures we may perform a balance of energy analysis for a selectively absorbing and emitting body exposed to solar radiation. In this analysis we will neglect the angular dependence of radiation properties. In other words, let us assume all surfaces to radiate isotropically in one hemisphere. If A_a is the effective surface absorbing solar radiation, and if $\mathcal{G}_\nu$ is the spectral irradiance of solar radiation at the surface of the absorber, the rate of absorption of energy must be

$$I_E^+ = A_a \int_0^\infty a_\nu \mathcal{G}_\nu \, d\nu \tag{16.20}$$

The absorptivity depends upon frequency and is denoted by a_ν. The emission from the surface obeys the relation derived in Equ.(7.55), again with the absorptivity (emissivity) taken as a function of frequency:

$$I_E^- = A \int_0^\infty a_\nu \mathcal{E}_{\nu b}(T) d\nu \tag{16.21}$$

A fraction a_ν of the spectral blackbody intensity is emitted at each frequency. Here, A is the emitting surface area, and T is the surface temperature of the body exposed to the Sun's radiation. This factor determines the spectral distribution of the radiation being emitted. Since $\mathcal{G}_\nu$ depends on the spectrum of solar radiation, the absorptivity does not drop out of the equations as in the case of gray bodies. As a result, the temperature attained by a selective surface strongly depends upon the average values of the absorptivity (or the emissivity) for the respective range of frequency of radiation (visible for the Sun's light, infrared for bodies at around room temperature).

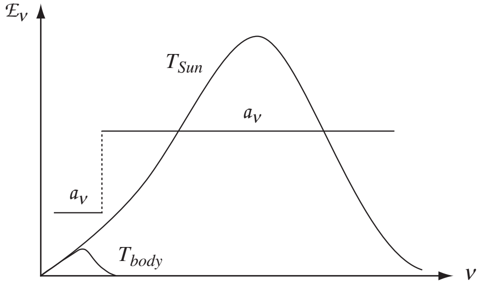

Figure 16.9: Spectrum of solar radiation and of infrared radiation emitted by a body exposed to the light of the Sun. The absorptivities (and therefore the emissivities) are taken to be different in the two distinct ranges of frequencies occupied by solar light and by infrared radiation.

16.2.2 A Daisy World

There is a nice example of a model of a planet where the presence of life leads to a self-regulating mechanism which keeps the temperature within a narrow range even though the sun is getting brighter all the time. The model is called a *daisy world*,[14] and it addresses the question of how the surface of the Earth could have had a relatively stable temperature over the course of billions of years, even though the radiation of the Sun must have increased considerably during the same period. This should have led to a steady increase of the surface temperature of our planet.

Imagine a planet without life circling the central star of the planetary system. The luminosity of the star is supposed to increase as a function of time. If the planet's surface has constant radiative properties, its temperature will increase in accordance with the

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[14] A.J. Watson and J.E. Lovelock (1983).

change of luminosity of the Sun (Fig. 16.10). Now assume that black daisies start growing, leading to an increase of the absorptivity at visible wavelengths: the planet will grow hotter than it otherwise would. Now, as the central star continues brightening, white daisies, which have a lower absorptivity, start replacing the black ones. This will tend to lower the temperature of the surface of the planet. All in all, it is possible to envisage a relatively simple model of a planet whose interaction with life leads to a surface temperature which stays within narrow bounds for quite a while.

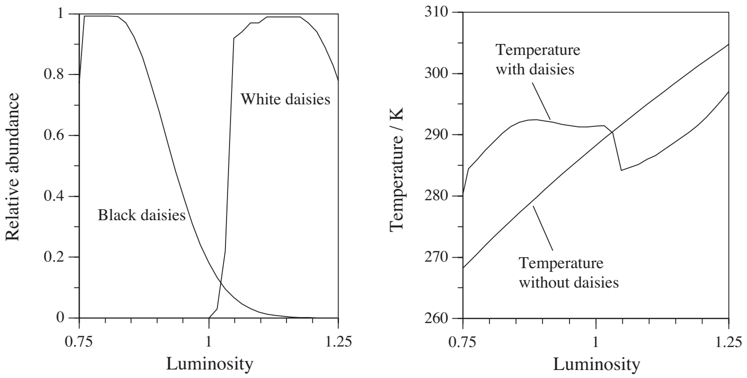


Figure 16.10: Simulation results of a simple model of a self-regulating daisy world. The radiative properties of the planet without life were taken as constant. The absorptivity in the visible part of the spectrum is taken to be larger for black daisies than for white ones, with the absorptivity of the dead surface somewhere in between. The emissivity at infrared wavelengths has been assumed to be the same for all three materials (black and white daisies, and rocks). As the central Sun gets brighter, first black daisies start to grow and cover the planet, making the surface warmer than it would otherwise be. As the luminosity of the Sun grows further, the black daisies get too hot, which lets them slowly die. White daisies, which do not get that hot in the same light, start growing later. As their number increases sharply, due to proper temperatures and increasing space on the planet, the average surface temperature first drops. Finally, it also gets too hot for the white daisies, leading to their demise. The temperature of the planet finally approaches that of the dead surface again. (This is an example of a simple system dynamics model created with Stella™. It consists of two first-order differential equations representing the laws of balance of the number of black and white daisies, respectively. The constitutive laws used are those for the temperature of the different types of surfaces, and laws governing the reproductive rates of the flowers.)

QUESTIONS

8. Is it possible to have surfaces that absorb solar radiation that tend to be cooler than the environment?
9. For the situation depicted in Fig. 16.9, do you expect the absorber to attain a temperature higher or lower than that of the environment?
10. Photovoltaic panels work better if they are cooler. What does this mean for the solar reflectance of the panel, and its infrared emittance?
11. Compare a body that is a perfect absorber and emitter to a body that is a perfect absorber for solar radiation but has a lower than perfect emittance for infrared radiation. What is the effect of the imperfection upon the entropy production rate in steady-state?

EXAMPLE 16.4. Temperature of absorbers on Earth.

Consider a flat disk and a piece of white paper both facing the Sun. The disk is made out of cast iron, for which the average absorptivity for solar radiation is 0.95. For the radiation emitted by the surface (at a temperature not far from 300 K) the value is 0.21. The sheet of paper has values of 0.28 and 0.95 for the absorptivities for solar radiation and for its own radiation, respectively (Table 7.3). Assume the bodies to emit radiation evenly from both surfaces. Consider radiation from the environment to be blackbody radiation at a temperature of 20°C. The irradiance of solar radiation is taken to be 800 W/m^2. What are the temperatures reached in the steady state by the surfaces if you neglect convection?

SOLUTION: The balance of energy takes a simple form. Since the absorptivities are constant (but different for absorption and emission), we get

$$A\,a_s\,\mathcal{G}_{sun} = a_b \sigma 2A\left(T_b^4 - T_o^4\right)$$

Since the temperature of the body will not be very different from that of the environment, we can assume the absorptivity to be the same for this component as for the radiation from the body itself.

We obtain the following numerical values for the surface made out of cast iron:

$$T_b = \left(\frac{a_s\,\mathcal{G}_{sun}}{2a_b\sigma} + T_o^4\right)^{1/4} = \left(\frac{0.95 \cdot 800}{2 \cdot 0.21 \cdot 5.67 \cdot 10^{-8}} + 293^4\right)^{1/4} \mathrm{K} = 445\mathrm{K}$$

For the piece of paper the result is quite different, due to the different values of the absorptivities:

$$T_b = \left(\frac{0.28 \cdot 800}{2 \cdot 0.95 \cdot 5.67 \cdot 10^{-8}} + 293^4\right)^{1/4} \mathrm{K} = 312\mathrm{K}$$

As we might have expected, the paper does not get as hot as the cast iron disk. Note that the environment has a relatively large influence upon the result, at least in the second case. Naturally, convection due to current of air flowing over the surfaces would prevent the bodies from getting as hot as calculated.

EXAMPLE 16.5. The Earth as a selective absorber.

(a) Model the surface of the Earth as a uniform selective absorber. With an average temperature of 15°C and an absorptivity for the Sun's light of 0.70, how large is the emissivity (absorptivity) at infrared wavelengths? (b) What is the expected effect of the increase of the amount of greenhouse gases in the atmosphere? (c) Different latitudes receive different amounts of radiation from the Sun in the course of the year. The following formula gives a rough representation of the actual values observed:

$$s(x) = 1 - 0.26\left(3x^2 - 1\right)$$
$$x = \sin\left(latitude\right)$$

$s(x)$ represents relative values so that the integral of $s(x)$ over the range of x is equal to 1. Model the temperature of the Earth as a function of latitude if you assume a constant absorptivity of 0.70 for the Sun's light, and a constant emissivity of 0.61 (calculated from the average values according to the first problem).[15] Assume that only radiation is responsible for the temperatures attained.

SOLUTION: (a) We can repeat the analysis of Example 7.12, this time with differing values for the absorptivities for emission and absorption. The balance of energy yields

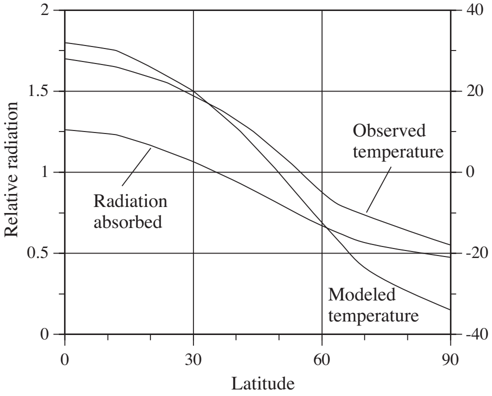
$$a_V \pi R^2 \mathcal{G}_{sc} = a_{IR} 4\pi R^2 \sigma T^4$$

where V and IR stand for visible and infrared, respectively; $\mathcal{G}_{sc}$ is the solar constant. The absorptivity (emissivity) in the infrared therefore must be

$$a_{IR} = \frac{a_V \mathcal{G}_{sc}}{4\sigma T^4} = \frac{0.70 \cdot 1360}{4 \cdot 5.67 \cdot 10^{-8} \cdot (273 + 15)^4} = 0.61$$

(b) The effect of the greenhouse gases can be modeled by lowering of the emissivity at infrared wavelengths.

Figure Ex.5



(c) If there is no other type of heat transfer in the latitudinal direction, there must be a balance of energy for each strip of constant latitude which takes the form

$$a_V s(x) \mathcal{G}_{sc} = a_{IR} 4\sigma T^4$$

We can solve this equation for different values of x to obtain the hypothetical latitudinal distribution of temperature (see the diagram).

If the modeled temperature distribution is compared to the measured average temperature as a function of latitude, it is observed that the actual values do not change as much over the globe as the numbers obtained from the model. Convective currents from the equator to the poles redistribute the entropy, making the temperature gradient from the equator to the poles much smaller.

16.3 CONCENTRATING SOLAR RADIATION FOR POWER ENGINEERING

Considering that direct solar radiation has a temperature nearly as high as the surface of the Sun suggests that we should be able to exploit sunlight as a high-temperature "fuel" with which bodies can be heated to hotnesses approaching that of the Sun. Solar energy engineering[16] and materials research could benefit from such a source.

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15. See R.S. Lindzen (1990) for a slightly different model and more details.

To heat a body to the temperature of the surface of the Sun we must place it in a radiation field similar to the one found there. The difference between direct solar radiation on Earth and the radiation at the surface of our star is not to be found in the intensity but rather in the angular distribution: on Earth, solar radiation comes from a small solid angle, while at the surface of the Sun it strikes the body from all directions of a hemisphere. The radiation field found there can be recreated here at the focus of an ideally concentrating mirror, and if you place the body at that focus, it will receive the kind of radiation needed for attaining the same high temperature. A simple argument shows how we can calculate the maximum concentration necessary for the desired application. Without concentration, a body having a surface perpendicular to the direct rays of the Sun receives an energy flux equal to $\Omega_s i_E$. Ideally, the energy flux should be $\pi\, i_E$. Therefore, we need a concentration C calculated according to

$$C_{max}\Omega_s i_E = \pi i_E \quad \Rightarrow \quad C_{max} = \frac{\pi}{\Omega_s} = 46200 \tag{16.22}$$

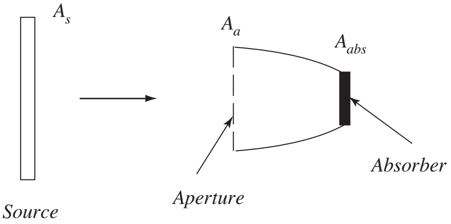

Figure 16.11: Radiation from a source can be concentrated by a device having an aperture and an absorber. The ratio of the surface areas of the aperture and the absorbing body is called the *concentration factor.*

Let us give a more careful thermodynamic argument of why the number just calculated corresponds to the maximum value of concentration of sunlight permitted by the law of balance of entropy.[17] Consider a setup as in Fig. 16.11, which concentrates the radiation from a source onto an absorber. First, the concentration factor of the concentrating device is defined by

$$C = \frac{A_a}{A_{abs}} \tag{16.23}$$

where A_a and A_{abs} are the surface areas of the aperture and the absorber, respectively. The largest possible concentration factor must be related to the highest possible temperature attained by a body receiving radiation from the sun. Now, from a balance of entropy performed for the bodies exchanging radiation we know that if radiation is transferred from body 1 to body 2, the rate of production of entropy is larger than zero—see Equ.(7.47)—and the temperature of the second body is smaller than that of

---

16. Detailed information on concentration of sunlight and on related optical problems in solar energy engineering can be found in the books by A. Rabl (1985, Chapter 5) and by J. Duffie and W. Beckman (1991, Chapter 7).

17. Note that the result depends upon the index of refraction of the medium through which the light travels before hitting the absorber. Therefore, higher values of concentration can be attained which do not violate the laws of thermodynamics.

the first. The highest possible value of the hotness of body 2 is reached when the rate of production of entropy vanishes, which is equivalent to saying that the temperatures of the bodies must have become equal and the net rate of transfer of energy must have dropped to zero.

We can express the energy currents flowing from one body to another in terms of the fraction $\mathcal{F}_{12}$ of the radiation emitted by the first of these bodies which is intercepted by the second.[18] If the surfaces radiate like black bodies, the energy current flowing from body 1 to body 2 will then be

$$I_{E,12} = \mathcal{F}_{12} A_1 \sigma T_1^4$$

Conversely, the energy flux leaving body 2 which is intercepted by body 1 will be expressed by

$$I_{E,21} = \mathcal{F}_{21} A_2 \sigma T_2^4$$

The condition of maximum concentration leads to equality of these expressions, which yields the important result

$$A_1 \mathcal{F}_{12} = A_2 \mathcal{F}_{21} \qquad \textbf{(16.24)}$$

We can apply this relation to the surface of the arrangement of source, aperture, and absorber shown in Fig. 16.11, to obtain

$$\begin{aligned} A_s \mathcal{F}_{s-a} &= A_a \mathcal{F}_{a-s} \\ A_s \mathcal{F}_{s-abs} &= A_{abs} \mathcal{F}_{abs-s} \end{aligned}$$

from which we conclude that the concentration factor can be calculated in terms of

$$C = \frac{\mathcal{F}_{s-a} \mathcal{F}_{abs-s}}{\mathcal{F}_{a-s} \mathcal{F}_{s-abs}}$$

In the case of maximal concentration, all the radiation entering the aperture should flow to the absorber; this requires the factors $\mathcal{F}$ for radiation from the source to the aperture and from the aperture to the absorber to be equal, resulting in

$$C = \frac{\mathcal{F}_{abs-s}}{\mathcal{F}_{a-s}}$$

For this ratio to be maximal, the factor $\mathcal{F}_{abs\text{-}s}$ which describes the flow of radiation from the absorber back to the source, must have its largest possible value which is obviously 1. This yields the result for the largest possible concentration factor:

$$C_{max} = \frac{1}{F_{a-s}} \qquad \textbf{(16.25)}$$

---

[18] If the radiation emitted by body 1 and received by body 2 gets there directly without intermediate reflection(s), this fraction is equal to the radiation shape factor introduced before in Section 12.1.2.

Note that the factor $\mathcal{F}_{a\text{-}s}$ must be the radiation shape factor $F_{a\text{-}s}$ since there are no intermediate reflectors between the source and the aperture. This shape factor has been calculated in Problem 3 of Chapter 12. The arrangement used there is equivalent to what we have in the case of the Sun aligned with a (small) circular surface directly facing our star. Obviously, the result is equal to the square of the sine of the half-angle θ_s subtended by the Sun for an observer on the Earth. Since we have to have a concentrator whose aperture sees only the Sun if we wish to obtain maximal concentration, this angle is equal to the acceptance half-angle θ_a of the optical setup. Therefore:

$$C_{max} = \frac{1}{\sin^2(\theta_a)} \tag{16.26}$$

This is indeed what we had derived before on the basis of the simple argument presented in Equ.(16.22).

EXAMPLE 16.6. Maximum concentration of line focus concentrators

Use arguments like those which led to Equ.(16.22) to show that the maximum concentration reached in a line focus concentrator is given by

$$C_{max} = \frac{1}{\sin(\theta_a)}$$

where θ_a is the acceptance half-angle of the concentrator. Calculate the corresponding value for direct sunlight.

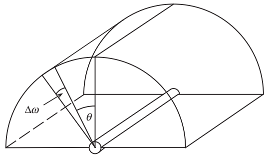

Figure Ex.6.1

SOLUTION: We should consider a thin long cylinder receiving direct sunlight from the narrow angle (0.5°) subtended by the sun. How much more light would it receive if we had isotropic radiation with the same intensity as that of direct solar light coming from the part or all of the upper half of a cylindrical dome as in the figure?

When working with linear concentrators, we have to deal with angles instead of solid angles. In reverting the flow of radiation, we can argue as follows: the light emitted by the cylindrical pipe in the center spreads into the upper half-space and over the dome. The flux of energy or entropy associated with this flow must be

$$j_x' = \int_{\cap} i_x \cos(\theta) d\omega$$

The factor $\cos(\theta)$ is a consequence of the projection of the radiation onto the plane receiving it. According to the geometry in the accompanying figure, this can be transformed into

$$j_x' = 2i_x \int_0^{\pi/2} \cos(\theta) d\theta = 2i_x$$

for isotropic radiation. If we have sunlight which comes only from a narrow angle ω_s flowing from all over the dome towards the pipe, the energy flux just calculated would correspond to C times the actual flux:

$$2i_E = C\omega_s i_E$$

Now, since the angle (not the solid angle) subtended by the Sun is $2R_s/d = 2\sin(\theta_a)$, where R_s and d are the radius and the distance of the Sun, respectively, we conclude that the concentration factor is indeed given by the formula presented above. For direct sunlight, the maximum possible concentration factor turns out to be 214.

EXAMPLE 16.7. Steady-state temperatures reached in a parabolic trough concentrator.

Consider an uncovered metal pipe having a radius of 4.0 cm at the center of a line focus parabolic concentrator. Take the concentrated light (with a concentration ratio 40) to be perfectly intercepted by the cross section presented by the pipe. (a) If only radiation is considered to cause heat loss, calculate the temperature reached by the pipe in the steady state. The pipe absorbs a fraction $(\tau\alpha) = 0.95$ of the incoming light, and its emissivity is 0.90 at infrared wavelengths. The irradiance onto the aperture of the concentrator is 900 W/m^2, and the ambient temperature is 20°C. (b) Calculate the width of the parabolic trough concentrator.

SOLUTION: (a) A simple balance of energy will deliver the temperature reached by the pipe absorbing concentrated solar light. In the steady state, we have

$$2rL(\tau\alpha)C\,\mathcal{G} = 2\pi rLe\sigma\left(T^4 - T_a^4\right)$$

which gives us

$$T = \left(\frac{(\tau\alpha)C\,\mathcal{G}}{\pi e\sigma} + T_a^4\right)^{1/4}$$

$$= \left(\frac{0.95 \cdot 40 \cdot 900}{\pi \cdot 0.90 \cdot 5.67 \cdot 10^{-8}} + 293^4\right)^{1/4} = 685\,\mathrm{K}$$

(b) Since the concentration is 40, the aperture, i.e., the width of the parabolic trough, must be 40 times as wide as the pipe. Therefore, the width is 3.2 m.

16.4 TRANSMISSION AND ABSORPTION IN FLAT-PLATE SOLAR COLLECTORS

The concepts of absorption, reflection, and transmission of radiation can be applied to a nice example in the field of solar energy engineering, namely the computation of the amount of light absorbed by a flat-plate collector. Consider a flat piece of metal (the absorber) covered by one or more sheets of glass, as in Fig. 16.12. The Sun's light is partly reflected, absorbed, and transmitted by the cover. Part of the transmitted radiation is reflected back through the cover, and the rest is absorbed, which is what we would like the collector to do. In general, the radiative properties needed here, i.e., the reflectance, absorptance, and transmittance,[19] all depend upon the frequency of the light; moreover, reflection and absorption properties also depend upon the angles of incidence. In the following development, we shall take these properties to be independent of wavelength, which for reflection and transmission of the cover, is quite correct for normal glass.[20] Also, the absorptance of the absorber will be assumed to be independent of the angles of incidence of radiation. Finally, we shall be working with effective angles of incidence for diffuse light, which allows us to deal with the problem in a simple manner.

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[19] Often, in engineering, the terms absorptance and emittance are used for absorptivity and emissivity, respectively, rather than for the rates of absorption and emission per unit area by a surface. See … for the original definitions.

[20] Duffie and Beckman (1991), Chapter 5.7.

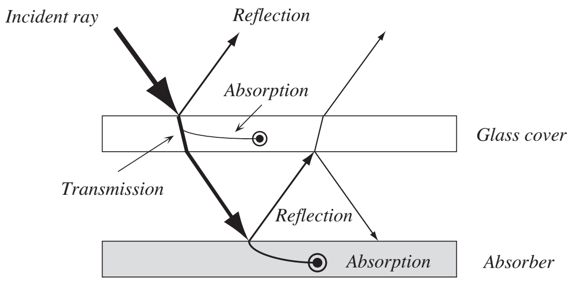

Figure 16.12: Light to be absorbed by a solar collector first has to pass through the cover system. Reflection and absorption by the glass cover reduce the amount of radiation incident upon the absorber.

16.4.1 The Transmittance-Absorptance Product of a Collector

Let us start with the final step in the chain of events leading to absorption of light. We introduce the effective transmittance τ of the cover system we are going to calculate later. If α is the absorptance of the absorber plate, a fraction $\tau\alpha$ of incident light is absorbed while the rest (which equals $(1-\alpha)\tau$), is reflected back up to the cover. Then, if ρ_d is the reflectance of the cover system for diffuse reflected light from the absorber, radiation with a relative intensity of $(1-\alpha)\tau\rho_d$ is reflected back down again in the direction of the absorber; see Fig. 16.12. This process continues infinitely many times leading to

$$(\tau\alpha) = \tau\alpha\sum_{i=0}^{\infty}\left[(1-\alpha)\rho_d\right]^i$$

for the effective transmittance-absorptance product. Note that $(\tau\alpha)$ should be considered as a new quantity and not as the product of τ and α. The result can be transformed to yield

$$(\tau\alpha) = \frac{\tau\alpha}{1-(1-\alpha)\rho_d} \tag{16.27}$$

16.4.2 Transmittance of the Cover Without Absorption

Transmittance through one or more sheets of glass is not equal to unity, even if we neglect absorption, because of the reflection of light at the surfaces of the covers. When a ray of light is refracted at the surface of a body, part of it is also reflected (see Fig. 16.13). The reflection depends both upon the nature of the refracting materials, i.e., upon the index of refraction n, and upon the nature of light, i.e., its state of polarization. It is common to split a ray of light into two plane polarized components, one perpendicular to the plane as in Fig. 16.13, the other parallel to that plane. The fraction of incident light of a particular reflected component is calculated according to[21]

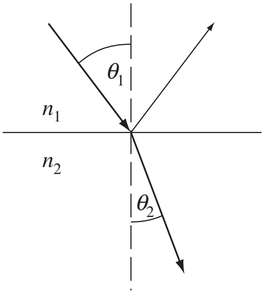

Figure 16.13: Refraction of light at an interface also leads to partial reflection.

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[21] For a derivation, see Siegel and Howell (1992), p. 102–108.

$$r_{\parallel} = \frac{\tan^2(\theta_2 - \theta_1)}{\tan^2(\theta_2 + \theta_1)}$$
$$r_{\perp} = \frac{\sin^2(\theta_2 - \theta_1)}{\sin^2(\theta_2 + \theta_1)} \tag{16.28}$$

for the parallel and the perpendicular components, respectively. If the incident light is unpolarized, the total reflection is equal to the average of the values calculated using the previous result:

$$r = \frac{1}{2}\left(r_{\parallel} + r_{\perp}\right) \tag{16.29}$$

Now, the transmittance τ of unpolarized light is not simply $1 - r$, since part of a transmitted ray is reflected back up at the second interface of a cover sheet (as in Fig. 16.14), and so on. This results in a total transmittance of

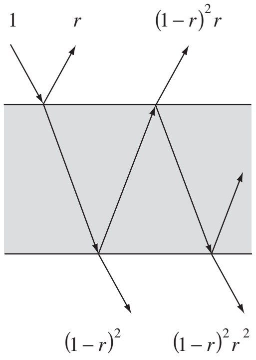

Figure 16.14: Multiple reflection and transmission of a ray of light in a sheet of glass; absorption is neglected. The total light transmitted is smaller than what passes through the first interface.

$$\tau_{\perp} = \left(1 - r_{\perp}\right)^2 \sum_{i=0}^{\infty} r_{\perp}^{2i} = \frac{\left(1 - r_{\perp}\right)^2}{1 - r_{\perp}^2} = \frac{1 - r_{\perp}}{1 + r_{\perp}} \tag{16.30}$$

for, say, the normal component of polarization. The other component is treated in the same manner. Therefore, our final result for the transmittance of a single nonabsorbing sheet of glass will be

$$\tau_r = \frac{1}{2}\left(\frac{1 - r_{\perp}}{1 + r_{\perp}} + \frac{1 - r_{\parallel}}{1 + r_{\parallel}}\right) \tag{16.31}$$

for unpolarized incident radiation; the index r reminds us that this is the transmittance due to reflection. For N identical covers the formula becomes

$$\tau_r = \frac{1}{2}\left(\frac{1 - r_{\perp}}{1 + (2N-1)r_{\perp}} + \frac{1 - r_{\parallel}}{1 + (2N-1)r_{\parallel}}\right) \tag{16.32}$$

16.4.3 Transmittance with Absorption in the Cover

The absorption of radiation in a cover sheet made of glass can be calculated in the same manner as was done with absorption of radiation in the Earth's atmosphere; see Section 16.1.2. The length of the path of light in a glass cover is $L/\cos(\theta_2)$ where L is the thickness of the cover. If κ is the coefficient of absorption (the extinction coefficient) in the glass, the transmittance due only to absorption is

$$\tau_a = \exp\left(-\kappa \frac{L}{\cos(\theta_2)}\right) \tag{16.33}$$

For N covers, we simply use N times the thickness L. Now, with the effect of absorption present, the equations for transmittance, reflectance, and absorptance of the cover system are more complicated than what we would have without this effect. (See

Problem 5.) A satisfactory approximation for solar collectors is the following:

$$\begin{aligned} \tau &\approx \tau_a \tau_r \\ \alpha &\approx 1 - \tau_a \\ \rho &\approx \tau_a (1 - \tau_r) \end{aligned} \tag{16.34}$$

This is a consequence of the fact that the transmittance due to absorption in the glass is nearly 1.

Transmission and absorption of diffuse radiation. Diffuse radiation, either scattered from the sky or reflected from the ground, cannot be handled that easily. To include these contributions to radiation, effective incidence angles should be introduced which can be used in the equations presented here. For diffuse light from the sky, an effective angle of 60° delivers satisfactory solutions for all slopes of collectors. (The slope is the angle between the plane of the collector and the horizontal.) For radiation reflected from the ground, however, the effective incidence angle used varies from 90° to 60° for collector slopes from 0° to 90°, respectively.[22]

EXAMPLE 16.8. Normal transmittance-absorptance product of a solar collector.

A collector with a single sheet of glass as a cover is oriented directly toward the sun. The glass has a thickness of 3 mm and an extinction coefficient of 12 m^{-1}. Its refractive index is 1.53. The absorptance of the absorber for solar light is 0.92. (a) Calculate the transmittance-absorptance product for direct light and for diffuse light from the sky. (b) What is the rate of absorption of sunlight by this collector (per surface area) if the direct and the diffuse irradiances are 600 W/m^2 and 400 W/m^2, respectively? (c) Consider direct radiation only and assume it to be blackbody radiation with a temperature of 5777 K; also assume that the radiation which is not absorbed by the collector is unaffected by transmission and reflection. Calculate the rate of production of entropy for the process of the interaction of the direct component of sunlight with the collector if the absorber is at a temperature of 70°C.

SOLUTION: (a) To find the desired result we need the quantities in Equ.(16.34) which means we have to compute the transmittances of the cover due to reflection and due to absorption. The angles of incidence of direct and of diffuse light are 0° and 60°, respectively. Therefore, we calculate the appropriate quantities for these two angles:

$$\begin{aligned} \tau_a(0) &= \exp(-\kappa L) = \exp(-12 \cdot 0.0030) = 0.965 \\ \tau_a(60) &= \exp(-\kappa L / \cos(60°)) = \exp(-12 \cdot 0.0030/0.5) = 0.931 \end{aligned}$$

We need Snell's law to calculate the reflection factors r at normal incidence and at 60°:

$$\frac{n_1}{n_2} = \frac{\sin(\theta_2)}{\sin(\theta_1)}$$

In the case of normal incidence we combine this law with Equ.(16.29). Let both angles θ_1 and θ_2 go to zero. In this limit, the parallel and the perpendicular components of r become

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[22] Duffie and Beckman (1991), p. 227.

$$r_{\parallel} = \frac{\tan^2(\theta_2-\theta_1)}{\tan^2(\theta_2+\theta_1)} \quad \rightarrow \quad \frac{(\theta_2-\theta_1)^2}{(\theta_2+\theta_1)^2}$$
$$r_{\perp} = \frac{\sin^2(\theta_2-\theta_1)}{\sin^2(\theta_2+\theta_1)} \quad \rightarrow \quad \frac{(\theta_2-\theta_1)^2}{(\theta_2+\theta_1)^2}$$

Therefore we have

$$r(0) = \frac{(\theta_2-\theta_1)^2}{(\theta_2+\theta_1)^2} = \frac{(\theta_2/\theta_1-1)^2}{(\theta_2/\theta_1+1)^2} = \frac{(n_1/n_2-1)^2}{(n_1/n_2+1)^2} = 0.044$$

At 60° incidence, θ_2 is 34.5°. The reflection coefficients turn out to be

$$r_{\parallel}(60) = \frac{\tan^2(-25.5)}{\tan^2(94.5)} = 0.00140$$
$$r_{\perp}(60) = \frac{\sin^2(-25.5)}{\sin^2(94.5)} = 0.187$$

The transmission coefficients due to the process of reflection now are calculated as

$$\tau_r(0) = \frac{1-r(0)}{1+r(0)} = \frac{1-0.044}{1+0.044} = 0.916$$

and

$$\tau_r(60) = \frac{1}{2}\left(\frac{1-r_{\perp}(60)}{1+r_{\perp}(60)} + \frac{1-r_{\parallel}(60)}{1+r_{\parallel}(60)}\right) = \frac{1}{2}\left(\frac{1-0.187}{1+0.187} + \frac{1-0.00140}{1+0.00140}\right) = 0.841$$

Now we are ready to calculate the approximate optical properties of the cover systems. According to Equ.(16.34) we obtain

$$\begin{aligned}
\tau(0) &\approx 0.965 \cdot 0.916 = 0.88\\
\alpha(0) &\approx 1-0.965 = 0.035\\
\rho(0) &\approx 0.965(1-0.916) = 0.081\\
\tau(60) &\approx 0.931 \cdot 0.841 = 0.78\\
\alpha(60) &\approx 1-0.931 = 0.069\\
\rho(60) &\approx 0.931(1-0.841) = 0.15
\end{aligned}$$

Equ.(16.27) allows us to compute the transmittance-absorptance products for the two incidence angles:

$$(\tau\alpha)_n = \frac{\tau(0)\alpha}{1-(1-\alpha)\rho_d(60)} = \frac{0.88 \cdot 0.92}{1-(1-0.92)0.15} = 0.82$$
$$(\tau\alpha)_{60} = \frac{\tau(60)\alpha}{1-(1-\alpha)\rho_d(60)} = \frac{0.78 \cdot 0.92}{1-(1-0.92)0.15} = 0.73$$

Note that the diffuse reflectance of the cover for light reflected from the absorber is equal to the value calculated for 60°.

(b) The rate of absorption of energy of the collector is calculated simply as the product of the transmittance-absorptance product and the irradiance:

$$\Sigma_E / A\big|_b = (\tau\alpha)_n \mathcal{G}_b = 0.82 \cdot 600\,\mathrm{W/m^2} = 492\,\mathrm{W/m^2}$$
$$\Sigma_E / A\big|_d = (\tau\alpha)_{60} \mathcal{G}_d = 0.73 \cdot 400\,\mathrm{W/m^2} = 292\,\mathrm{W/m^2}$$

(c) If we wish to consider only the first part of the interaction of sunlight with the collector, we may simply assume heat loss and removal of heat not to be present. (The total rate of production of entropy due to all processes will certainly be larger than the number calculated here.) The law of balance of entropy for the absorber then takes the form

$$\dot{S} = I_{S,in} - I_{S,reflected} + \Pi_S$$

where

$$\dot{S} = \frac{1}{T_c}\dot{E}$$
$$I_{S,in} = \frac{4}{3}\frac{1}{T_s} I_{E,in}$$
$$I_{S,reflected} = \frac{4}{3}\frac{1}{T_s} I_{E,reflected}$$

T_c and T_s are the temperature of the absorber and of solar radiation, respectively. Therefore, the rate of production of entropy per unit surface due to solar radiation is given by

$$\begin{aligned}\Pi_S / A &= \frac{1}{T_c}(\tau\alpha)_n \mathcal{G}_b - \frac{4}{3}\frac{1}{T_s}(\tau\alpha)_n \mathcal{G}_b \\ &= \frac{1}{273+70} 0.82 \cdot 600\,\mathrm{W}\big/\left(\mathrm{K}\cdot\mathrm{m}^2\right) - \frac{4}{3}\frac{1}{5777} 0.82 \cdot 600\,\mathrm{W}\big/\left(\mathrm{K}\cdot\mathrm{m}^2\right) \\ &= 1.32\,\mathrm{W}\big/\left(\mathrm{K}\cdot\mathrm{m}^2\right)\end{aligned}$$

Because of the high temperature of solar radiation, incident sunlight delivers only a small part of the entropy which appears in the absorber as the result of absorption. The loss of available power due to this process alone reaches almost 400 W/m^2 (for 20°C ambient temperature).

EXERCISES AND PROBLEMS

1. Calculate the normal spectral irradiance for solar radiation at the distance of the Earth for a blackbody spectrum of temperature 5777 K. (Normal means for a plane perpendicular to solar rays.)
2. Integration of the spectral entropy intensity of solar radiation according to the WRC spectrum (Fig. 16.3) yields a value of 4620 W/(K · m^2 · sr), while the integral value of the energy intensity is $2.011 \cdot 10^7$ W/(m^2 · sr). Derive the equivalent blackbody temperature and calculate the entropy current density for such radiation near the Earth.
3. An experiment on the disinfection of water using solar radiation showed[23] that a dose of 2000 kJ/m^2 of radiation in the wavelength band between 350 nm and 450 nm was required to kill bacteria in a particular sample. Estimate how long the sample has to be exposed to sunlight at midlatitudes around noon on a clear day in summertime.

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[23] Wegelin et al. (1994).

4. Calculate the steady-state temperature reached by a cylindrical absorber at the line focus of a parabolic trough concentrator. Assume that the absorber is surrounded by a glass pipe and that convective losses from the surface of the pipe have to be taken into account. (See Example 16.7 and Problem 12 in Chapter 7.)

5. Show by use of ray-tracing techniques such as the one used in Section 16.4, that the transmittance, reflectance, and absorptance of the glass cover of a flat-plate solar collector are given by

$$\tau_\perp = \tau_a \frac{\left(1 - r_\perp\right)^2}{1 - \left(r_\perp \tau_a\right)^2}$$

$$\rho_\perp = r_\perp + \frac{\left(1 - r_\perp\right)^2 \tau_a^2 r_\perp}{1 - \left(r_\perp \tau_a\right)^2}$$

$$\alpha_\perp = \left(1 - \tau_a\right) \frac{1 - r_\perp}{1 - r_\perp \tau_a}$$

for the component of light which is polarized at right angles to the plane of incidence (Fig. 16.13). Show that Equ.(16.34) is a good approximation to these equations.

6. Consider the absorptance of cavities and rooms. Light falls from the outside on the opening of a cavity (which might be a room with a window for the opening). The surface area of the opening is A_a, while the area of the inner surfaces is A_i. The absorptance of the inner walls is assumed to be α_i (independent of the angle of incidence and the wavelength). (a) Show that the total absorptance is given by

$$\alpha = \alpha_i \left[\alpha_i + \left(1 - \alpha_i\right) \frac{A_a}{A_i} \right]^{-1}$$

if the opening is not covered. (*Hint:* Consider rays bouncing off the interior walls and assume that after each reflection, there is a probability of A_a/A_i for the ray to escape through the hole.) (b) Show that the result must be

$$\alpha = \tau \alpha_i \left[\alpha_i + \left(1 - \alpha_i\right) \tau_d \frac{A_a}{A_i} \right]^{-1}$$

if there is a window with a transmittance to direct light τ and a transmittance to diffuse reflected light from the interior of τ_d.

7. For the collector and the situation discussed in Example 16.8, estimate the rate of production of entropy due to heat loss to the ambient if the energy current due to this effect is 40% of the irradiance. Compare this value to the rate of production of entropy due to absorption by the collector.

APPENDIX

1 List of Tables

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APPENDIX 1

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APPENDIX 2

LIST OF SYMBOLS

The following tables list the most important symbols used in the text, along with their meanings and their units. The last column of each table identifies the chapter in which the symbol was introduced.

Table S.1	Symbols using latin letters
Table S.2	Symbols using greek letters
Table S.3	Subscripts and superscripts

TABLE S.1: Symbols using latin letters

Symbol	Meaning	SI-units
a	Steffan-Boltzmann constant	$J \cdot m^{-3} K^{-4}$
A	Surface area, cross section	m^2
$\mathcal{A}$	Rate of absorption of radiant energy per unit area	$W \cdot m^{-2}$
a	Absorptivity	
$\mathbf{B}$	Magnetic flux density	T
c	Speed of sound, speed of light	$m \cdot s^{-1}$
c , c_V	Specific temperature coefficient of energy	$J \cdot K^{-1} kg^{-1}$
c_P	Specific temperature coefficient of enthalpy	$J \cdot K^{-1} kg^{-1}$
$\bar{c}_P$	Molar temperature coefficient of enthalpy	$J \cdot K^{-1} mole^{-1}$
$\bar{c}_V$	Molar temperature coefficient of energy	$J \cdot K^{-1} mole^{-1}$
$\bar{c}$	Concentration	$mole \cdot m^{-3}$
C	Coulomb (unit of electrical charge)	
C	Capacitance (electrical)	F
C	Temperature coefficient of energy	$J \cdot K^{-1}$
C	Concentration ratio	
COP	Coefficient of performance	
C_f	Friction coefficient	
C_P	Temperature coefficient of enthalpy	$J \cdot K^{-1}$

TABLE S.1: Symbols using latin letters

Symbol	Meaning	SI-units
C_V	Temperature coefficient of energy	$J \cdot K^{-1}$
C_V	Hydraulic capacitance	m^3Pa^{-1}
C'	Momentum capacitance per length	$kg \cdot m^{-3}$
C^*	Ratio of capacitance rates	
Ct	Carnot (unit of heat—entropy)	
°C	Degrees Celsius	
d_{ij}	Components of the velocity gradient tensor (symmetric part)	s^{-1}
D	Diffusion constant	m^2s^{-1}
e	Specific energy	$J \cdot kg^{-1}$
$\bar{e}$	Molar energy	$J \cdot mole^{-1}$
E	Energy of system (energy content)	J
E	Young's modulus	$N \cdot m^{-2}$
E_{chem}	Energy exchanged (transported) in chemical process	
E_{el}	Energy exchanged in electric process	J
E_{mech}	Energy exchanged in mechanical process	J
E_{th}	Energy exchanged in thermal process (heating and cooling)	J
$\mathbf{E}$	Electric flux density	$V \cdot m^{-1}$
$\mathcal{E}$	Emissive power (rate of radiant energy emitted per unit area)	$W \cdot m^{-2}$
$\mathcal{E}_b$	Emissive power of black body	$W \cdot m^{-2}$
f	Degrees of freedom	
f_Q	Specific source rate of quantity Q	
$\mathbf{F}$	Force (flux of momentum)	N
F_{12}	Radiation shape factor	
F'	Solar collector efficiency factor	
F_R	Solar collector heat removal factor	
$\mathcal{F}$	Faraday's constant	$C \cdot mole^{-1}$
g	Gravitational field strength	$N \cdot kg^{-1}$
G	Gravitational constant	$N \cdot m^2kg^{-2}$
G	Conductance	
G_E	Energy conductance	$W \cdot K^{-1}$
G_S	Entropy conductance	$W \cdot K^{-2}$
G_V	Hydraulic conductance	$m^3Pa^{-1}s^{-1}$
G	Gibbs free energy	J

TABLE S.1: Symbols using latin letters

Symbol	Meaning	SI-units
$\mathcal{G}$	Irradiance (rate of incident radiant energy per unit area)	$W \cdot m^{-2}$
$\mathcal{G}_{sc}$	Solar constant	$W \cdot m^{-2}$
h	Height	m
h	Specific enthalpy	J/kg
$\bar{h}$	Molar enthalpy	$J \cdot mole^{-1}$
h	Planck's constant	$J \cdot s$
h	Overall heat transfer coefficient with respect to energy	$W \cdot K^{-1}m^{-2}$
h	Convective heat transfer coefficient with respect to energy	$W \cdot K^{-1}m^{-2}$
h_S	Overall entropy transfer coefficient	$W \cdot K^{-2}m^{-2}$
H	Enthalpy	J
$\mathbf{H}$	Magnetic field strength	$A \cdot m^{-1}$
i_S	Entropy intensity of radiation	$W \cdot K^{-1}m^{-2}s^{-1}$
$i_{S\nu}$	Spectral entropy intensity (with respect to frequency)	$W \cdot K^{-1}m^{-2}s \cdot sr^{-1}$
$i_{S\lambda}$	Spectral entropy intensity (with respect to wavelength)	$W \cdot K^{-1}m^{-2}m^{-1}sr^{-1}$
i_E	Energy intensity of radiation	$W \cdot m^{-2}sr^{-1}$
$i_{E\nu}$	Spectral energy intensity (with respect to frequency)	$W \cdot m^{-2}s \cdot sr^{-1}$
$i_{E\lambda}$	Spectral energy intensity (with respect to wavelength)	$W \cdot m^{-2}m^{-1}sr^{-1}$
I	Current; flux	
I_E	Flux of energy	W
I_L	Flux of angular momentum	$kg \cdot m^2s^{-2}$
I_m	Flux of gravitational mass	$kg \cdot s^{-1}$
I_{mag}	Hertz magnetic current	A
I_n	Flux of amount of substance	$mole \cdot s^{-1}$
I_p	Flux of momentum	N
I_Q	Flux of electrical charge	A
I_S	Flux of entropy	$W \cdot K^{-1}$
I_V	Volume flux	m^3s^{-1}
J	Joule (unit of energy)	
j	Flux density	
$\mathbf{j}$	Flux density vector	
j_E	Energy flux density	$W \cdot m^{-2}$

TABLE S.1: **Symbols using latin letters**

Symbol	Meaning	SI-units
j_p	Momentum flux density	$\mathrm{N \cdot m^{-2}}$
j_S	Entropy flux density	$\mathrm{W \cdot K^{-1} m^{-2}}$
$\mathcal{J}_p$	Momentum current density tensor	$\mathrm{N \cdot m^{-2}}$
k	Boltzmann's constant	$\mathrm{J \cdot K^{-1}}$
k_E	Thermal conductivity with respect to energy	$\mathrm{W \cdot K^{-1} m^{-1}}$
k_S	Thermal conductivity with respect to entropy	$\mathrm{W \cdot K^{-2} m^{-1}}$
K	Kelvin (unit of temperature)	
K	See Greek letter kappa	
$\mathcal{K}_p$	Chemical equilibrium constant	
l , L	Length	m
l_f , l_v	Specific entropy of fusion (vaporization)	$\mathrm{J \cdot K^{-1} kg^{-1}}$
$\bar{l}_f$, $\bar{l}_v$	Molar latent entropy of fusion (vaporization)	$\mathrm{J \cdot K^{-1} mole^{-1}}$
L	Electrical inductance	H
L	Luminosity of star	W
L_V	Hydraulic inductance	$\mathrm{Pa \cdot s^{2} m^{-3}}$
L'	Momentum inductance per length	$\mathrm{N^{-1} m^{-2}}$
$\mathcal{L}$	Loss of available power	W
m	Meter (unit of length)	
m	Mass of a body	kg
m_a	Air mass	
mole	Unit of amount of substance	
M_0	Molar mass	$\mathrm{kg \cdot mole^{-1}}$
n	Amount of substance	mole
$\mathbf{n}$	Unit normal vector on surface (directed outward)	
N_A	Avogadro's constant	
N	Newton (unit of momentum flux—force)	
Nu	Nusselt number	
NTU	Number of transfer units	
$\mathbf{p}$	Momentum	$\mathrm{N \cdot s}$
P	Pressure	Pa
$\mathcal{P}$	Power	W
$\mathcal{P}_{av}$	Available power	W
$\mathcal{P}_{diss}$	Rate of dissipation of energy	W
Pa	Pascal (unit of pressure)	
Pr	Prandtl number	
q	Specific enthalpy of fusion	$\mathrm{J \cdot kg^{-1}}$

TABLE S.1: **Symbols using latin letters**

Symbol	Meaning	SI-units
q_n	Molar enthalpy of fusion	$\mathrm{J \cdot mole^{-1}}$
Q	Electrical charge	C
Q	Substancelike quantity	
q	Specific quantity	
r	Radial variable	m
r	Specific enthalpy of vaporization	$\mathrm{J \cdot kg^{-1}}$
r	Specific rate of absorption of energy	$\mathrm{W \cdot kg^{-1}}$
R	Universal gas constant, 8.31 J/(K · mole)	$\mathrm{J \cdot K^{-1} mole^{-1}}$
R	Electrical resistance	Ω
R	Radius	m
Re	Reynolds number	
R_E	Thermal resistance with respect to energy	$\mathrm{K \cdot W^{-1}}$
R_S	Thermal resistance with respect to entropy	$\mathrm{W^{-1} \cdot K^{2}}$
R_m	Specific gas constant	$\mathrm{J \cdot K^{-1} kg^{-1}}$
R_V	Hydraulic resistance	$\mathrm{Pa \cdot s \cdot m^{-3}}$
s	Second (unit of time)	
s	Entropy per mass (specific entropy)	$\mathrm{J \cdot K^{-1} kg^{-1}}$
$\bar{s}$	Molar entropy	$\mathrm{J \cdot K^{-1} mole^{-1}}$
S	Entropy; entropy content of a body	$\mathrm{J \cdot K^{-1}}$
S_e	Entropy exchanged in a process	$\mathrm{J \cdot K^{-1}}$
S_{gen}	Amount of entropy produced in a system	$\mathrm{J \cdot K^{-1}}$
t	Time	s
T	Ideal gas temperature, absolute temperature	K
$\mathcal{T}$	Conductive part of momentum current density tensor (stress tensor)	$\mathrm{N \cdot m^{-2}}$
u	Specific internal energy	$\mathrm{J \cdot kg^{-1}}$
U	Voltage	V
U	Internal energy	J
U	Overall heat transfer coefficient	$\mathrm{W \cdot K^{-1} m^{-2}}$
U_{mag}	Magnetic tension	V
u	Specific energy, internal energy per mass	$\mathrm{J \cdot kg^{-1}}$
v	Velocity	$\mathrm{m \cdot s^{-1}}$
V	Volume of a body	$\mathrm{m^3}$
w	Amount of precipitable water	
W	Watt (unit of energy flux or power)	
W	Width	m

TABLE S.1: Symbols using latin letters

Symbol	Meaning	SI-units
x	Position variable	m
x	Quality	
y	Mole fraction	
z	Vertical distance	m
z	Ionization number of atom	

TABLE S.2: Symbols using Greek letters

Symbol	Meaning	SI-units
α	Absorptivity (absorptance)	m^2s^{-1}
α	Peltier coefficient	$J \cdot K^{-1} C^{-1}$
α	Thermal diffusivity	
α_l	Linear temperature coefficient of expansion	K^{-1}
α_R	Linear temperature coefficient of electrical resistance	K^{-1}
α_V	Temperature coefficient of expansion of volume	K^{-1}
α_μ	Temperature coefficient of chemical potential	$mole \cdot K^{-1}$
β	Temperature coefficient of pressure	K^{-1}
β_E	Scattering coefficient	m^{-1}
β_μ	Pressure coefficient of chemical potential	$mole \cdot Pa^{-1}$
γ	Adiabatic exponent, ratio of entropy capacities	
$\gamma\,'$	Polytropic exponent	
γ	Volume coefficient of thermal expansion	K^{-1}
δ	Kronecker symbol	
ε	Heat exchanger effectiveness	
ε	Seebeck coefficient	$V \cdot K^{-1}$
η	Efficiency	
η_c	Carnot efficiency	
η_{I}	Thermal efficiency, first law efficiency	
η_{II}	Second law efficiency	
θ	Celsius temperature	°C

TABLE S.2: Symbols using Greek letters

Symbol	Meaning	SI-units
κ	Specific entropy capacitance	$\mathrm{J \cdot K^{-2} kg^{-1}}$
$\bar{\kappa}$	Molar entropy capacitance	$\mathrm{J \cdot K^{-2} mole^{-1}}$
κ	Bulk viscosity	$\mathrm{Pa \cdot s}$
κ_E	Absorption coefficient	$\mathrm{m^{-1}}$
κ_S	Adiabatic compressibility	$\mathrm{Pa^{-1}}$
κ_T	Isothermal compressibility	$\mathrm{Pa^{-1}}$
K	Entropy capacitance	$\mathrm{J \cdot K^{-2}}$
K_V	Entropy capacitance at constant volume	$\mathrm{J \cdot K^{-2}}$
K_P	Entropy capacitance at constant pressure	$\mathrm{J \cdot K^{-2}}$
λ	Wavelength	m
λ^X	Lagrange multiplier for quantity X	
Λ_V	Latent entropy with respect to volume	$\mathrm{J \cdot K^{-1} m^{-3}}$
Λ_P	Latent entropy with respect to pressure	$\mathrm{J \cdot K^{-1} Pa^{-3}}$
μ	Viscosity	$\mathrm{Pa \cdot s}$
μ	Chemical potential	$\mathrm{G = J \cdot mole^{-1}}$
μ	Attenuation coefficient	$\mathrm{m^{-1}}$
μ_o	Permeability constant	$\mathrm{H \cdot m^{-1}}$
ν	Frequency	$\mathrm{s^{-1}}$
ν	Kinematic viscosity	$\mathrm{m^2 s^{-1}}$
ν	Stoichiometric coefficient	
π	Volume density of rate of production	
π_S	Volume density of rate of production of entropy	$\mathrm{W \cdot K^{-1} m^{-3}}$
Π	Rate of production	
Π_n	Rate of production of amount of substance	$\mathrm{mole \cdot s^{-1}}$
Π_S	Rate of production of entropy	$\mathrm{W \cdot K^{-1}}$
ρ	Density (general)	
ρ	Mass density of a body	$\mathrm{kg \cdot m^{-3}}$
ρ	Reflectivity (reflectance)	
ρ_E	Energy density	$\mathrm{J \cdot m^{-3}}$
ρ_S	Density of entropy of body	$\mathrm{J \cdot K^{-1} m^{-3}}$
σ	Steffan-Boltzmann constant	$\mathrm{W \cdot m^{-2} K^{-4}}$
σ	Volume density of source rate	
σ_E	Volume density of source rate of energy	$\mathrm{W \cdot m^{-3}}$
σ_S	Volume density of source rate of entropy	$\mathrm{W \cdot K^{-1} m^{-3}}$
Σ	Source rate	
Σ_E	Source rate of energy	W

TABLE S.2: **Symbols using Greek letters**

Symbol	Meaning	SI-units
Σ_S	Source rate of entropy	$W \cdot K^{-1}$
τ	Time constant	s
τ	Transmittance	
τ	Quantum of amount of substance	mole
τ	Relaxation time	s
$(\tau\alpha)$	Transmission-absorption product	
υ	Specific volume (inverse density)	m^3kg^{-1}
$\overline{\upsilon}$	Molar volume	m^3mole^{-1}
φ	Potential	
ϕ	Relative humidity	
Ω	Ohm (unit of electrical resistance)	
ω	Angular velocity	s^{-1}
ω	Humidity ratio	

TABLE S.3: **Subscripts and superscripts**

Symbol	Meaning
a	Air
a	Ambient
a	average
ad	Adiabatic
av	Available
b	Body
b	Beam
b	Blackbody
c	Carnot
C	Capacitive
(c)	Conductive (part of a) flux
chem	Chemical
cond	Conductive
conv	Convective

TABLE S.3: **Subscripts and superscripts**

Symbol	**Meaning**
d, diff	Diffuse
e	Exchanged
el	Electrical
eq	Equilibrium
E	Energy, with respect to energy
E	Equilibrium
EC	Electro-chemical
f	Final
f	Fluid, solvent
f	Fusion
f	Formation
g	Gas, gaseous, vapor
gen	Generated
grav	Gravitation
GC	Gravito-chemical
h	Horizontal
H	High (high temperature, temperature of furnace…)
hp	Heat pump
hydro	Hydraulic
i	Initial
in	In, flowing inward
kin	Kinetic
l	Liquid
l	Linear
L	Angular momentum
L	Inductive
L	Low (low temperature, temperature of cooler…)
m	Mass
m	Mean
mag	Magnetic
max	Maximum
mech	Mechanical
min	Minimum
net	Sum, total (net current)
o , 0	Reference point
o , out	Out, flowing outward

TABLE S.3: Subscripts and superscripts

Symbol	Meaning
p	Momentum, with respect to momentum
p	Absorber plate
P	Pressure, with respect to pressure, at constant pressure
Q	Charge
Q	With respect to quantity Q
r	Radiation
rad	Radiative
$refr$	Refrigerator
R	Resistive, electrical resistance
S	Entropy, with respect to entropy
s	Surface
s	Sun, solar
s	Solid
s	Solute
s	Storage, store
t	Top
th	Thermal
TE	Thermo-electric
v	Vaporization, vapor
V	Volume, hydraulic, with respect to volume, at constant volume
wb	Wet bulb
x,y,z	Spatial coordinates, with respect to spatial coordinate
λ	With respect to wavelength
ν	With respect to frequency

APPENDIX 3

GLOSSARY

The following short glossary is provided because the generalized version of thermodynamics presented in this book requires a generalization of and sometimes a change from usual terminology. Only the most important terms are included. Expressions in italics can be found elsewhere in the glossary.

Amount of substance Formal measure of an amount of substance as used in the sense of chemistry (the “number of moles”, the “number of particles”).

Availability The amount of energy that can be released (see *release of energy*) in the fall of *entropy* from points of high to points of low *temperature*. Quite generally, the amount of energy that can be released in the fall of a *fluidlike quantity* through a potential difference.

Balance of energy Application of the general *law of balance* to *energy*.

Balance of entropy Application of the general *law of balance* to *entropy*.

Binding energy Binding energy to the current of a fluidlike quantity which thereby is lifted from a lower to a higher *potential*. Same as *using energy*. Opposite of *releasing energy*.

Caloric Used as an alternative term for *heat*. The caloric theory of heat can be rendered formal and correct in a modern sense if it is accepted that caloric is not conserved (that it can be produced). In this case it turns out to be equivalent to the *entropy* of a body.

Chemical driving force The difference of the *chemical potential*.

Chemical potential The *potential* associated with processes which have to do with the change or the flow of *amount of substance*.

Continuous processes Processes which are spatially continuous, i.e. processes in which the variables change from point to point inside a body or a system.

Constitutive relations The laws which are not generic but differentiate between bodies and circumstances. (Generic laws see *laws of balance*)

Current Informal term for the phenomenon of the transport of a *fluidlike quantity*. Also used colloquially for the formal measure which is called *flux*.

Current density Formal measure of the local condition of a current. The *flux* is the surface integral of the current density. For a scalar *fluidlike quantity*, the current density is a vector.

Density Spatial density of a *fluidlike quantity*. The integral of the density of such a quantity over the volume of a system delivers the amount of the fluidlike quantity stored in the system.

Dissipation rate Rate at which energy is bound (see *binding of energy*) as the result of the *production* of *entropy.*

Dissipative process A process during which *entropy* has been produced, i.e. an *irreversible process*.

Driving force Informal term for the difference of a *potential*. The thermal driving force is the difference of the thermal potentials at two points in space, i.e. the difference of *temperatures*.

Dynamics A theory of dynamics requires the formulation of the *laws of balance* and the *constitutive relations* appropriate for a particular case. Models of dynamical processes rely upon the clear distinction between laws of balance and the constitutive relations.

Energy Quantity that accompanies all physical processes and takes the same role in all of them. Used to quantify the coupling of processes (*releasing energy*). Flows together with *fluidlike quantities* in conductive processes (*energy carrier*).

Energy carrier *Fluidlike quantity* (in conductive processes).

Energy current The amount of energy crossing the surface of a system in unit time as the result of a transport process. It must be distinguished from *power.*

Entropy Formal for a quantity of *heat* or *caloric*. Entropy is the *fluidlike quantity* of thermal processes and thus obeys a *law of balance*. It can be stored (see *heat function*), it can flow (*entropy current*), and it can be created (see *production*).

Entropy current Measure of the transfer of *entropy* across the surface a a system.

Entropy production The process of the *production* of *entropy* as the result of an *irreversible process*.

Entropy production rate The rate at which *entropy* is produced in an *irreversible process*.

Exchanged quantity The amount of a *fluidlike quantity* which has crossed the surface of a system together with a *current* in a certain interval of time. Formally equal to the integral of the *flux* over time.

Extensive quantities Quantities which scale with the size of a system are said to be extensive. The *fluidlike quantities* are a subset of the extensive quantities. An example of a non-fluidlike extensive quantity is provided by the volume.

First law of thermodynamics The *law of balance* of energy. It includes only rates of change of the energy content, energy *currents*, and energy *source rates*.

Fluidlike quantities Physical quantities which possess a *density* and a *current density* (and possibly *source densities* and *production densities*) are called fluidlike. *Laws of balance* can be written for them. They form a subset of the *extensive quantities*. The classical fluidlike quantities are momentum, angular momentum, *entropy*, charge, amount of substance, and (gravitational) mass.

Flux Formal measure of the amount of a *fluidlike quantity* crossing the surface of a system in unit time (informally, the same quantity is called a *current*). The flux is counted as positive for a current flowing out of the system.

Flux density The surface density of a *flux*. The surface integral of a flux density delivers the flux. Equivalent to *current density.*

Heat Informal term for *entrop*y. Equivalent to *caloric*. (Commonly the energy *exchanged* in *heating* is called heat; this usage is not followed in this text.)

Heating The process of the transfer of *heat* (*entropy*) across the surface of a body excluding convective transports. The opposite process is cooling.

Heat capacity Used in the sense of *entropy* capacitance, i.e. as the derivative of the entropy function with respect to temperature. The usual "heat capacities" are called the *temperature coefficients of energy* and *of enthalpy.*

Heat function The formal expression of the assumption that a body contains a certain amount of *heat*, where the heat stored is a function of the independent variables describing the properties of the body. This heat function turns out to be equivalent to the *entropy* of the body.

Hotness The hotness manifold is the primitive concept for describing the ordering of bodies according to the sensation of how hot they are. The numerical measure of the hotness is the *temperature*.

Intensive quantities The quantities which remain the same if a body is divided into parts. A subset of the intensive quantities are the *potentials*.

Irreversible process A process which leads to the *production* of *entropy.*

Irreversibility Opposite of *reversibility.* The condition of irreversibility means that *entropy* is produced during a process.

Law of balance The formal relation which holds for the rate of change of the *fluidlike quantity* of a body and its currents (and possibly its *source rates* and *production rates*).

Level Informal term for *potential*. Levels are the conjugate quantities (conjugate with respect to energy) of the *fluidlike quantities*.

Minimization of entropy production Minimizing *irreversibility* is achieved by minimizing the rate of *production* of *entropy.*

Potential Formal term for the quantities which take the role of physical *levels*, otherwise known as the *intensive quantities*. There is a potential associated with each of the *fluidlike quantities*. The classical potentials are velocity (for momentum), angular velocity (for angular momentum), temperature (for *entropy*), the electrical potential (for charge), the *chemical potential* (for *amount of substance*), and the gravitational potential (for gravitational mass).

Potential difference Difference of *potential* at two points in space.

Power The rate of *release of energy* or the rate of *binding of energy.* Power is associated with an internal process as opposed to an external process (i.e. a transport process which is quantified by *energy current*s).

Power of heat Colloquial for the *power* associated with the fall of *entropy* from points of higher to points of lower temperature. This is Carnot's *puissance du feu*. Integrating the power of heat over time delivers the *availability.*

Production Informal term for the phenomenon of production of a *fluidlike quantity.* A quantity which is produced can accumulate inside a system even without being transported into the system. Production (or destruction) is associated with nonconservation of a quantity.

Production rate Formal measure of the production of a *fluidlike quantity.* It describes the amount of the quantity produced inside a system per unit time. A negative production rate means the quantity is destroyed.

Production (rate) density The spacial density of the *production rate*. Its volume integral delivers the production rate.

Releasing energy Release of energy when the current of a *fluidlike quantity* goes from higher to lower *potential*. Opposite of *binding of energy.*

Reversibility The condition of reversibility means that there is no *entropy production* during a process.

Second law of thermodynamics The *law of balance* of *entropy.* (Historically, it is not clear what to call the Second law of thermodynamics; in traditional thermodynamics, we find countless forms of the Second law. Here, the simplest and—for us—most useful choice has been made.)

Source Informal for processes as by which a *fluidlike quantity* is transferred into a system without having to cross the surface of the systems. This happens as the result of the interaction of bodies and fields.

Source rate Formal measure of a *source* of a *fluidlike quantity.* It determines the amount of the quantity delivered to the system per unit time.

Source (rate) density The spatial density of the *source rate*. Its volume integral delivers the source rate.

Superconducting process A transport process of a *fluidlike quantity* which does not require a *driving force*.

Temperature Measure of the *hotness* of a body. *Temperature* is like the coordinate on the hotness manifold. Temperature serves the role of the thermal *potential*.

Temperature coefficient of energy The derivative of the energy with respect to temperature at constant volume. Normally called *heat capacity at constant volume*.

Temperature coefficient of enthalpy The derivative of the enthalpy with respect to temperature at constant pressure. Normally called *heat capacity at constant pressure*.

Thermostatics Theories of thermostatics try to derive the conditions pertaining only to static thermal situations. Usually, these conditions are derived by maximizing or minimizing functions such as the *entropy* or the energy of a system.

Uniform processes Spatially uniform processes, i.e. processes in which variables of a system have the same value at every point at a given moment.

Using energy Same as *binding of energy.*

Appendix 4

Answers to Questions

Chapter 4

Note: If the term *heat* is used, it is used in the sense of entropy.

1. Different size bodies.
2. *T* measures how warm an object is.
3. Thermal capacitance of the body of water f must be higher than that of the piece of copper.
4. Temperature difference is driving force for flow, flow is in direction of decreasing *T*.
5. No, heat can also melt a body. No, we can compress air.
6. *T* changes independently of changes of heat.
7. Heat can be produced or taken from the environment. For the body, it does not matter where heat comes from.
8. Energy for pumping heat (like pumping water). More energy is needed to pump additional heat.
9. Looks analogous to electricity ($\mathcal{P} = UI_Q = U^2/R$). We assume that the heat flow is proportional to ΔT.
10. Fire, flow of electricity, friction, chemical reactions, absorption of sunlight, diffusion of substances.
11. All processes except for the production of heat can be reversed.
12. No heat flow. Heat inside air has been compressed into smaller space.
13. Could change by more because of production of entropy.
14. The rate at which energy is needed to pumped the entropy (not equal to the rate at which energy is made available).
15. Thermal power is the same.
16. Thermal power: 1.0 W. Used inside the battery.
17. For an element of the bar, the thermal power is ΔT multiplied by the local entropy current.
18. 24 kg.
19. Ohm's law and capacitive relation.
20. Hot water in the environment has a cooling curve analogous to the one found in discharging of a capacitor.
21. It freezes and boils. Its density has a maximum at 4°C.
22. Pressure of the ideal gas. Pressure is absolute, electric, gravitational potentials, and speed are not. (See also Question 9.)
23. In a voluntary process, energy is released. There is no other process than dissipation.
24. No.
25. Yes (example: expansion of air).
26. Upward to the right.
27. The gas has to be heated to keep its temperature.
28. Horizontal to the left. Entropy of system decreases. Entropy is communicated to environment.
29. Thermal energy currents are added.
30. Engine gets more efficient.
31. See Question 9.
32. Ct = J/K, W/K, W/K.
33. 5000 W/K.
34. 0.5. 0.3/0.5 = 0.6.
35. Difference of thermal energy currents equals thermal power.
36. Since $\mathcal{P}_{diss} = T\Pi_S$, the relevant temperature difference is $T - 0$.
37. 1.0 W/K. 1.0 W/K and 400 W.
38. 20 W/K.
39. They are equal.
40. It is defined as the useful (= thermal)

power divided by the energy current from the heater (rather than the useful power divided by the thermal power).

41. 10.
42. Loss of power is always positive, and it is proportional to the entropy production rate.
43. Otherwise, entropy production rates would be undetermined.
44. Entropy added to a material can also lead to changes of volume. Temperature can also change as a result of expansion or compression.
45. Linear measure *TS* relation. Yes.
46. 7.7 J/(K^2kg).
47. Zero.
48. 1400 J/K. 420 kJ.
49. Since $k = c/T$ with c = const. Or it leads to Equ.(4.40) with c = const.
50. Increases. Decreases.
51. It varies as the inverse of temperature. Take the derivative of Equ.(4.42) with respect to temperature.
52. Heating and cooling of simple bodies in an environment of constant temperature (*T* behaves like *U* of a capacitor).
53. Energy is released in the fall of entropy from high to low T; if there is no other obvious process, the energy is dissipated.
54. It increases by 100%.
55. A junction is not considered a storage element for entropy, so the steady-state balance applies.
56. The actual temperatures matter.
57. Because of entropy production.
58. Entropy would not flow (could neither enter nor leave the engine).
59. The fall of entropy through a part of the total temperature difference is assumed to be reversible. The model can be quite useful for real engines.
60. Entropy is absorbed and emitted at constant temperatures.
61. The transport of entropy with charge is assumed to be non-dissipative.
62. Entropy flows conductively from hot to cold, reducing the effect of pumping.

CHAPTER 5

1. Entropy of steam and water together decreases, entropy of environment increases.
2. Wax melts, absorbing entropy from the water without changing its temperature.
3. Only if the substance is not flowing into or out of the control volume.
4. Yes, phase change by itself is reversible.
5. The energy added is part of the change of the energy of the system; another part is related to the change of volume.
6. Roughly 550 J/(K·kg).
7. More entropy can be stored in a given volume. Phase change temperature should be in the range of temperatures required for hot water.
8. Because *T* is constant (see Equ.(5.4)).
9. Both temperature and volume can change.
10. The entropy that leads to a volume change at constant *T*, per unit volume.
11. The entropy that leads to a change of temperature at constant *V*, per unit temperature.
12. Constant pressure heating.
13. It takes less entropy to change the temperature of air at constant volume.
14. Constant *p* curve is less steep.
15. The entropy in the gas is compressed into a smaller volume. For a formal answer, see Equ.(5.39).
16. Close to adiabatic.
17. Isothermal compression give larger change of V (entropy is emitted by the air).
18. The compression is close to adiabatic which makes the air hot. This in turn makes the pump hot: non-adiabatic phase of cooling of air.
19. When $dV/dt = 0$, we have $dT/dt = 0$. With $I_S \neq 0$, the condition no longer holds.
20. Latent entropy with respect to volume is positive ($T > 4$°C) or negative (0°C $< T < 4$°C). Adiabats have a minimum (Fig. 5.13).
21. The difference of the entropy capaci-

tances at constant p and constant V is *R/T*.

22. Take values for O_2 and N_2: $c_V = 2.5R$, $c_P = 3.5R$. Adiabatic exponent: 1.4.
23. Heat transfer produces entropy.
24. Entropy is exchanged between the dry part and the water vapor component.
25. Processes undergone by the materials modeled here are reversible.
26. $0 = TdS/dt - PdV/dt$.
27. $c_P/c_V = (T\kappa_P)/(T\kappa_V)$.
28. $\Delta E = C_V(T_2 - T_1)$. $\Lambda_V = P/T$, and Equ.(5.66). Alternatively: C_V is the temperature coefficient of energy, and the energy of the ideal gas only depends upon temperature.
29. Part of it is emitted to the environment as a consequence of expansion. Energy stored = energy absorbed – $P\Delta V$.
30. – 10 kJ.
31. Entropy is absorbed at temperatures lower than the highest one, and emitted at temperatures higher than the lowest one.

CHAPTER 6

1. Smaller amount of substance means smaller pressure.
2. More than twice as much H_2 than O_2, H_2 will be left over.
3. See Fig. 6.1 and interpretation given there.
4. Compare to two communicating containers containing fluids of different densities.
5. Energy is released by chemical reactions, used to pump electric charge. Batteries do not get fresh fuel.
6. First reaction emits entropy, second reaction takes entropy from its environment.
7. Chemical potentials of water and (saturated) vapor are equal.
8. Temperature of boiling point rises.
9. 18 g.
10. 0.091
11. 500 moles of H_2 , 250 moles of O_2 gas, 500 moles of water.
12. 0.0060 mole/min. 0.46 g/min, – 0.184 g/min, 0.28 g/min.
13. $1.0 \cdot 10^{-6}$ mole/s.
14. Higher chemical potential in air (it will flow into water, since there is 4 times more toluene in water in equilibrium).
15. Changes of *all* chemical potentials have to be considered to find the chemical potential difference at higher *T*.
16. Driving force is negative potential difference. Compare to voltage in electricity.
17. The chemical potential difference of a transformation has to be equal to zero in equilibrium.
18. Boiling point is lowered. Chemical potential of air decreases.
19. Energy is released; energy is used. Charging a battery.
20. Chemical power in reactions would not be definite if potential were not absolute.
21. Substances A and B are destroyed and make energy available (according to their amounts); this energy is used by C (according to its amount).
22. Power equals difference of all energy currents going in and all energy currents going out.
23. Voltage across terminals drops. OC voltage is not affected (no reactions).
24. Entropy is emitted, entropy is absorbed.
25. Yes, entropy of products must be smaller than entropy of reactants.
26. Entropy of products must be smaller than entropy of reactants.
27. Substance and charge must be directly coupled.
28. Gravitochemical potential is constant.
29. Logarithmic dependence.
30. Chemical potential of CO_2 is smaller in water (having no CO_2). Use chemical equilibrium.
31. Depends upon its molar fraction.
32. Diffusion.
33. Pressure and chemical potential of the liquid are lowered.
34. Salt dissociates into two ions.
35. The chemical potential of the liquid is lowered; at the original boiling point,

vapor condenses. Effect of change of μ is larger for salt.

36. For given driving force ($\Delta\mu$), the current depends upon how much substance there is to be transported.
37. Smaller than 1?
38. The net flux becomes zero.
39. μ of water is proportional to its pressure.
40. There is always solute in the cells. The difference of water pressure (osmotic pressure) does not go to zero.
41. Both phenomena are caused by the respective chemical potential difference which takes the same form. Equ.(6.75) and Equ.(6.88).
42. Third order (quadratic in the concentration of hydrogen, linear in the concentration of oxygen).
43. Exponential decaying to zero.
44. Concentration of B remains (almost) constant.
45. The chemical driving force is logarithmic but the concentrations are exponentials as functions of time.
46. Product concentration is small. Product concentration is large. Concentrations of products and reactants are comparable. Transfer of a substance between identical environment.
47. – 1415 J/mole.

CHAPTER 7

1. Temperature difference. Pressure difference.
2. No. Specific entropy of water remaining in tank stays constant.
3. Current of entropy: distributed over a surface; entropy source rate: distributed over a volume.
4. In the former case, entropy is not produced, it is only transported.
5. Yes, and yes.
6. 25 W/K.
7. Because of entropy production.
8. For the second material: slower reaction to changes.
9. No.
10. Convective mixing.
11. Different temperatures, different (thickness of) boundary layer.
12. It increases in thickness. Temperature decreasing toward the plate.
13. With 10 cm thickness, neglecting convection would lead to an error of about 20%.
14. Transfer resistances from water to metal and through metal are very small.
15. The expression for conduction contains the thickness of the layer, the expression for convection does not.
16. Radiation flows in different directions at a point in space. Emission and absorption are volumetric processes.
17. Radiation is more like convection (depends upon storage density of entropy). Yes.
18. The current of entropy away from the body is larger than the source (sink) rate in the body (by a factor 4/3).
19. 20
20. 19 of 20 units of what flows away are produced.
21. Yes, the temperature is still the same (see Equ.(7.33) and Equ.(7.34)).
22. In parallel.
23. Not for a gray surface. Yes, for a selective surface.
24. Yes (Table 7.3).

CHAPTER 8

1. Specific entropy does not change. Specific entropy is reduced.
2. Its speed.
3. Pressure (and possibly speed and gravitational potential) also factors in.
4. Flow of energy stored in compressed spring. Energy flow due to pushing the spring.
5. They are equal if the volume of the substance cannot change.
6. First, T_1 will decrease, T_2 will stay constant. Later, T_1 will stay constant and T_2 will increase.
7. Different phenomena (pushing fluid versus compressing it).
8. The effect mentioned here does not

necessarily lead to motion of the center of mass.

9. Specific quantities refer to a part of the fluid—we move with the fluid.
10. Pressure does not change.
11. They can be changed if the temperature changes with pressure.
12. Use the temperature coefficient of the chemical potential at standard conditions, and add the entropy related to the temperature change.
13. Entropy transfer is reversible too (the fluid receives entropy at the proper temperature everywhere). In our model, dissipation is due to the fact that we treat the fluid as uniform.
14. Equ.(8.70): fluid flowing in is at the same pressure as fluid already present.
15. Relaxation of pressure: energy is released and dissipated. Second term in Equ.(8.74).
16. Liquid flows in through a throttle.
17. The fluid in the tank gets hotter every day: collector losses increase.
18. With stratified water, cooler water returns to collector, making the collector more efficient. Mixing leads to higher losses in the collector.

CHAPTER 9

1. Entropy that is produced has to be emitted to the environment and takes energy with it.
2. Only if there is a single constant temperature of the environment that receives the rejected entropy.
3. In fuel cells, the reactions run without entropy production (theoretically).
4. Yes. They use entropy that is already available in the environment.
5. Higher losses means more entropy production.
6. The cyclic operation of the fluid in the engine works reversibly. The fluid undergoes heating and cooling at constant temperatures.
7. Entropy needs temperature differences to flow into and out of the engine.
8. $\eta_{CA} = 29\%$.
9. Flow speed increases which makes the heat transfer from absorber to fluid more efficient.
10. Yes.

CHAPTER 13

1. (a) Entropy density; (b) entropy current density; (c) entropy production density.
2. Introduce a negative sign in the surface integral (Equ.(13.5)).
3. Because of entropy production.
4. Sources: entropy flows from somewhere else.
5. Three. For (a) entropy density, (b) entropy current density, (c) entropy production rate density.
6. Entropy flows in the direction of decreasing temperature.
7. Yes; introduce Fourier's law.
8. k_E has to be constant.
9. Equilibrium relations: no flows as independent variables (only T, P…).
10. Example: energy released in a flow of entropy through a temperature difference is used to drive a flow (dissipation) and to change the flow (inertia).
11. So that the entropy production rate will certainly be positive or zero.
12. Use Peltier element between two bodies of water at equal temperatures. Measure rates of change of T in terms of I_Q.
13. Charged particles flow through different materials.
14. A combination of electro-chemical potential with temperature (Equ.(13.70)).
15. Non-dissipative transport of charge and entropy; dissipative conduction.
16. Transport of entropy with charge in one direction; conduction in the other direction. Coupled transport has to be stronger than conduction.
17. Two sources of irreversibility: conduction of entropy and of charge.
18. $j_Q dT/dx$ can be positive or negative, so these terms must represent non-dissipative processes. Dissipation means entropy production.

CHAPTER 14

1. Divide Equ.(14.1) by T_s.
2. Equations for developed flow.
3. Two pressure terms (including longitudinal friction), two shear friction terms.
4. For given geometry, flow behavior depends on the dimensionless groups only.
5. Difference between incoming and outgoing radiative fluxes. See Answer to Question 17., Chapter 7.
6. Steady-state and no loss from fluid to environment.
7. Yes.
8. The collector's capacitance is much smaller than that of the storage element.
9. Equ.(14.26) includes $T_{f,in}$ which is the temperature of the water in the tank. In Equ.(14.26), the spatial temperature variation is treated properly.
10. Entropy transfer through ΔT. Ideal: no entropy loss to the environment.
11. Increase NTU.
12. Average ΔT is smaller.
13. Two counteracting effects are needed.

CHAPTER 15

1. All of entropy, not all of the energy.
2. They are equal.
3. Along horizontal (constant T) lines in the liquid-vapor area.
4. Equ.(15.15).
5. Smaller (smaller μ because of $\phi < 1$, equal h).
6. Molar mass of moist air is lower (M_0 of water is low). Moist air rises.
7. Equal temperatures, ideal gas model.
8. The stream of air has to remain in the adiabatic saturator long enough.
9. Evaporation as diffusive (conductive) transport of vapor through air: see conduction of charge or entropy.
10. Single-dimensional steady-state flow of a non-reacting species.
11. Transform the argument of the logarithm in Equ.(15.43).
12. Temperature decreases, humidity increases. More evaporation means more mixing means more dissipation.
13. Small temperature differences.
14. No dissipation between plant and environment. This is violated noticeably in the condenser.
15. From the values pertaining to saturated liquid and saturated vapor.
16. It separates mixtures if liquid and vapor from liquid or vapor.
17. It remains constant.
18. Specific entropy s is constant, so μ increases with pressure, see Equ.(15.53).
19. The volume is independent of temperature (Equations (15.55) and (15.56)).
20. Saturated vapor will partly condense.
21. Entropy is produced in the valve.

CHAPTER 16

1. Radiant power: solar constant multiplied by surface of sphere surrounding Sun having radius equal to Sun-Earth distance. Temperature from black-body radiation law.
2. Surface temperature from Fig. 16.1, use black-body radiation law.
3. Above the Earth's atmosphere.
4. Distance of air crossed by Sun's rays if the Sun is vertically above us.
5. Constant attenuation coefficient.
6. Treat radiation as a thermal system and use basic thermodynamic relations (Part III).
7. Temperature gives us the incoming entropy and energy, allows calculation of dissipation.
8. Selective absorber with low solar absorptivity and low infrared emissivity.
9. Temperature will be higher than that of the environment.
10. This effect does not have anything to do with reflectance and emittance. Losses and dissipation are temperature dependent.
11. T of imperfect emitter is higher, entropy production rate is lower.

APPENDIX 5

SOME SOLUTIONS OF END OF CHAPTER PROBLEMS

CHAPTER 1

1. dV/dt = – 0.010 m3/s. (a) IV3 = 0.0125 m3/s – 10^–4 m3/s2 · t. (b) 0.10 m3.
2.
3.
4. CV = A/(2·ρ·g)
5. (a) IV = 4.81·10^–6 m3/s. (b) PA = 1.0 bar, PB = 1.0078 bar, PC = 1.027 bar, PD = 1.0 bar. (c) Exponential functions approaching h = 0.20 m with a time constant of 208 s.
6.
7. (a) Two tanks connected by pipe, additional pipe for outflow, valves for each pipe. (c) dV1(t)/dt = - IV1, INIT V1 = C1*p1_init, dV2(t)/dt = IV1 - IV2, INIT V2 = C2*p2_init, IV1 = delta_pR_1/R1, IV2 = IF (TIME > 50) THEN delta_pR_2/R2 ELSE 0, delta_pC_1 = V1/C1, delta_pC_2 = V2/C2, delta_pR_1 = delta_pC_1-delta_pC_2, delta_pR_2 = delta_pC_2. (d) UC2 mirrors the UC1, time constant of 6.0 s. (e) 1.5·10^–4 F. (f) 100 kΩ. (g) IV1 = 0 A, IV2 = 2.0·10^–5 A, dUC1/dt = 0 V/s, dUC2/dt = – 0.133 V/s.
8.
9. (b) dM/dt = P – V, dP/dt = Diff/L, Diff = E – M; First equation: Law of balance. Second equation: analogous to law of induction. Diff: analogous to pressure difference. Unit (dimension) of L: time squared. (e) Undamped Oscillation, Period = 2π SQRT(L).
10. (a) IL starts at 0, IC becomes negative.

CHAPTER 2

1. PPump = 3.02 kW.
2. (b) Vf^2/(2CV). Energy is stored in the system.
3.
4.
5. (a) Uf = U1i·C1/(C1+C2), Q1f = U1i·C1^2/(C1+C2), Q2f = U1i·C1·C2/(C1+C2). (b) No. (c) Two communicating tanks, energy loss because of friction when water flows.
6. (a) IQ(t) = – |UB|/R·exp(–t/tau). (c) PB = – 0.86 W, PR = 0.44 W, PC = 0.42 W. (d) IE_BC = 0.86 W, IE_CR = 0.44 W. (e) 0.42 W. (f) Depends upon emission of heat.
7.
8. (a) 1.25·10^14 J. (b) 8.75·10^14 J. (c) 40 MW, 30 MW. (d) 8.75·10^14 J. (e) 4·10^15 J (in Switzerland).
9.
10. (a) 62.5·10^9 J. (b) 0.20 m3/s.
11. (b) 0.13 J. (c) 0.13 J. (d) E_diss = 0.050 J. (e) 1.34 s ≤ t ≤ 1.45 s, 0.065 J.
12.

CHAPTER 3

1.
2.
3. Positive source rate of momentum, negative current through rope. Free-body diagram: Force of gravity FG, Force of rope FR, FG = Sigma_p, FR = Ip.
4. djp/dx = ρ·g. jp(x) = ρ·g·(– L + x).
5.
6. (a) Larger change of speed belongs to smaller glider. (b) 3.1·10^–3. (c) 0.419 N. (d) Radiative (source rate).
7.

8. (a) 10^6 N/m. (b) 0.314 s. (c) Shortening of springdamping force points in the direction of force of spring. Stretching of spring: damping force points opposite to force of spring. This explains the jump of the acceleration of the car at about 1.04 s. 10^5 N.
9. (a) 0.944 N, – 3.78 N. (b) 77.7 N, – 17.66 N.
10. – 4.21 N.
11. (a) dp/dt = (v + vg)·Im. (b) v(m) = v0 + |vg|·ln(m0/m) and m(t) = m0 – |Im|·t.
12. v(t) = v0·exp(–|Im|/m·t).
13. (a) Mass is changing. (b) 18 9 m/s^2, 54.2 m/s^2. (c) 1280 m/s.
14.
15. Δr·tau/(2π·r^3·l·omega).
16. Lp = 1/D (D: spring constant). Omega = 1/SQRT(CpLp) = SQRT(D/m).
17.
18.
19. 560 N.
20. ΔE = 1/2·D·stretching^2.

CHAPTER 4

1.
2.
3.
4.
5. The bodies get heavier and more inert, i.e., their mass increases. We do not know if the body has become hotter or faster.
6.
7. Commonality: can be stored and can flow.
8.
9. ± 6.2·10^7 N/m^2.
10. 50·10^–6 K^–1.
11. 461°C.
12.
13. (a) dS/dt = IS_in, ΔS = Se,in. (b) dS/dt = Π_S – IS_out, ΔS = Sprod – Se,out. (d) dS/dt = Π_S. (f) dS_stone/dt = – IS1, dS_cont/dt = + IS2 – IS3, |IS2| > |IS1|. (g) 0 = Π_S – IS_out.
14. IS_net = 100 W/K. dS/dt = 100 W/K.
15. (a) Absorbed: 2250 J/K, emitted: 3000 J/K. (b) – 750 J/K. (c) – 750 J/K.
16. (a) – 70 W/K + 5.0 W/(K·s)·t. (b) – 1000 J/K, – 400 J/K.
17.
18. (b) Entropy is produced, so more entropy and energy are emitted to the environment.
19. (a) 2.04 W/K. (b) 2.27 W/K.
20. (a) dS/dt = IS. (b) dS/dt = Π_S.
21. 0.055 W/K.
22. 1.4·10^–8 W/K.
23. (b) 3.33·10^6 W/K. (c) 5.56·10^6 W/K, 3.33·10^9 W. (d) 2.22·10^6 W/K. (e) 7.78·10^6 W/K.
24. (b) 444 W/K. (c) 267 kW. (d) 444 W/K, 133 kW. (e) 300 kW. (f) 556 W/K.
25. (a) 1.02 W/K. (b) 281 W. (c) 0.38.
26. (a) 0.625 W/K. (b) 147 W. (c) Entropy is produced because of entropy transfer in the insulation of the freezer, and in the heat exchangers of the heat pump. (d) 0.171 W/K.
27.
28. B is better by a factor of 4.
29.
30. (a) 0.135 W/K. (b) 103 J/K.
31. 940 J/K and 345 kJ.
32.
33. 1/2·K·(Tf^2 – Ti^2).
34. 60.7 MJ.
35.
36.
37. (a) 36 kJ/K^2 and 10.8 MJ/K. (b) 10.1 W/K. (c) 101 W. (d) 371 W.
38. (a) 1200 W/(K·m^2). (b) – 100 kJ and 100 kJ. (c) 1.0·10^–3 W/K^2.
39. 1190 J/(K·kg), 0.175 W/(K·m). Entropy related values: 4.0 J/(K^2kg), 5.8·10^–4 W/(K^2m).
40. (a) IS = 0. (b) Yes, because of entropy transfer. (d) 2.0 W/K. (e) dT1/dt = – 0.0286 K/s, dT2/dt = 0.0429 K/s, dT3/dt = – 0.0143 K/s. (f) Final temperature: 50 °C, time constants of the order of 1000 s.
41. (b) roc_P = T_diff/tA. (d) dP/dt + (TH–TC)/tA·P = (TD–TC)/tA. (e) 1.25 s. (f) Like charging of a capacitor, final

temperature: 40°C.

42. (a) 3.41·10^–3 W/K. (b) 4.7·10^–3 W/K (electric fraction: 0.73). (c) 0.073 W. (d) 0.073 W / 1.53 W = 0.048.
43. (a) 0.30 W/K. (b) 0.014 W/K.
44. (a) Hot water: dS/dt = – IS_Peltier – IS_loss + Π_S_mixing. (b) – 0.034 K/s and 0.029 K/s. (c) 0.20 W/K. (d) 𝒫 = 1.07·10^–4 W/K^2 · ΔT^2. (f) 𝒫_el = 0.50 W, 𝒫_th = 12 W, efficiency: 4%.

CHAPTER 5

1. (a) IE_th / dn/dt / T. (b) 1230 J/(K·kg).
2.
3. (a) 7.0 g/s. (b) 3 g/s.
4. (a) 0.822 W/K. (b) – 1.15·10^–4 kg/s. (c) – 0.108 W/K. (d) 6210 J/(K·kg).
5. 946 m^3.
6. 0.0405 m.
7.
8. (a) – 1.73 kJ. (b) Se = – 5.77 J/K.
9. f = 2π·SQRT(γ·P·A^2/(m·V)).
10. (a) 1.21. (b) – 0.90·CV/T. Entropy is injected into the gaseous component when the temperature decreases.
11. ρ = b·T^n (n = 1/(γ* – 1)); P = B·ρ^(1+1/n).
12. E_comp = CV·(Tf – Ti).
13.
14. (b) γ = (Pi – P0)/(Pf – P0). (c) Energy of the gas is the same if the temperature is the same.
15. (a) Change of volume; – 50 kJ. (b) Heating; + 50 kJ. (c) Only energy exchanged in heating can be shown.
16. ΔE = T·ΔS – P·(Vgas – V liquid); 2.09 kJ. (See also Table 15.1.)
17. 2°C: dE/dt < 0. 20°C: IE,mech < 0, IE_th > 0; cannot be decided on the basis of what we know at this point.
18. (a) 4.92 MJ. (b) 10^6 Pa. (c) IE_mech = – nRT / (V1 + dV/dt·t) · dV/dt, dV/dt = – 1.93 m^3/s, V1 = 21.4 m^3.
19. 154.3 J/(K·mole).
20.
21. 8°C.
22.
23. No heating, no friction. dS/dt = 0. dE/dt = IE,comp. = – P·dV/dt. Energy decreases.
24.
25.
26. Function shifts to the left.
27. All the entropy stays in the body; ΔE / E_th = 1/γ.
28.
29. (a) 39.7 mole; 1.15 kg. (b) 3.47·10^–4 W/K. (c) 2.87 J/K^2; 4.01 J/K^2. (d) 8.65·10^–5 K/s.
30. (a) – 2.14 kJ. (b) 5.36 J.
31. (a) 2.9 mm. (b) 37.5 mJ.
32.
33. P = 5·10^14 Pa, T = 2·10^7 K, Pr = 4·10^13 Pa = 0.08 P.
34. (a) Entropy of universe turns out to be constant. (b) 1/10^4. (c) R(t)/R0 = ρ_rad,0/ρ_matter,0 · ρ_matter/ρ_rad; densities are comparable at a zize 10^4 times smaller than today.
35. (a) V·T^3 = V0·T0^3, γ = 4/3. (b) E_th_isothermal = 4/3·a·T^4·ΔV, E_mech_isothermal = – 1/3·a·T^4·ΔV; ΔE = a·T^4·ΔV.
36. (b) P = 2/3·ρ_E. (c) CV = 3/2·n·R.
37.
38. Statics: computation of equilibrium states. Dynamics: requires "equations of motion.," i.e., combinations of the balance of entropy in dynamical form and constitutive relations.

CHAPTER 6

1.
2. – 1.3 mole/min (consumption).
3.
4. – 394.4 kG.
5.
6. Gaseous (200, 300, 400 K): – 210.1, – 229, –247.8 kG. Liquid: –230.3, –237« –244.3 kG. Solid: – 232.2, – 236; – 241.2 kH.
7.
8. (a) 1.7. (b) – 1320 G.
9. (a) CH4 + 2O2 → Co2 + 2H2O. (b) 2744.5 J/(K·mole). (c) – 242.64 J/(K·mole). (d) – 2987 J/(K·mole) (emit-

ted). (e) – 890 kJ/mole. (f) – 55.6 MJ/kg.

10. 8.64·10^–14 J = 0.54 MeV.
11. – 237 kJ/mole.
12. 49.6 kPa.
13.
14. 1 / 1.3·10^26.
15. 3.7.
16.
17. 1.35 bar.
18. 9.40·10^(–6) mole/L and 12.8·10^(–6) mole/L.
19. 10^(–7) mole/L; pH = 7.
20.
21. (a) 25.6 bar. (b) 260 m.
22. 2.56·10^9 W.
23. Δs = + 43.34 J/(K·mole); s_prod = 30.60 J/(K·mole); endothermic.
24. – 1.9°C.
25. Yes. Δμ(25°C) = – 9.12 kG, Δμ(45°C) = – 9.99 kG.
26.
27. Fraction of NH3 increases with increasing pressure.
28. (a) Ice: 41.5 J/(K·mole), water : 63.3 J/(K·mole); – 136 bar/K. (b) – 138 bar/K.
29. (a) Hg gas condenses. (b) 0.27 Pa. (c) 22 mg/m^3. 0.2 h per week. (d) 1.5 times higher.
30. Density of entropy production rate: R·D / c · (dc/dx)^2.
31.
32.
33. Ag-108: Half life = 143.7 s, N0 = 53600. Ag-110: Half life = 22.4 s, N0 = 22800.
34.
35. (a) nA_final = 1.5 mole, nB_final = 0, nC_final = 0.5 mole. (b) dnA/dt = InA – V·k·cA·cB^2; dnB/dt = InB – 2·V·k·cA·cB^2; dnC/dt = – InC + V·k·cA·cB^2. (c) InA = 1.0 mole/h, InB = 2.0 mole/h; nA(equ) = 20 mole, nB(equ) = 3.536 mole.

CHAPTER 7

1. (a) 1.0 W/K. (b) dS/dt ≥ 1.0 W/K. (c) – 1.0 W/K; no (conductive) fluxes.
2. (a) – 400 K/m. (b) jS = 800 W/(K·m^2), jE = 3.2·10^5 W/m^2, kE = 800 W/(K·m). (c) – 0.80 W/K.
3. 203 W. The energy current decreases when a mineral deposit builds up.
4.
5. (a) 18.1 kW. (b) 9.6 m.
6. (a) 463 K. (b) 334 K.
7.
8. T_Sirius = 9100 K.
9. (a) 4.1·10^14 W/K. (b) 2.8·10^13 W/K. (c) 3.82·10^14 W/K. (d) 5.17·10^14 W/K.
10. (a) 120 W. (b) C·dT/dt = alpha·G_Sun – A·h·(T – Ta) – A·σ·(T^4 – Ta^4) – efficiency·G_Sun. (c) 0.56 K/s. (d) 331.4 K. (e) $\mathcal{P}$_el_final = 78 W.
11.
12. h(300 K) = 5 W/(K·m^2), h(500 K) = 11 W/(K·m^2), h(800 K) = 32 W/(K·m^2).
13. 105 min.
14. 1.3 days.
15. (a) 4.85·10^4 s. (b) 2.09 W/K. (c) 0.78·10^5 J/K. (d) 22.7 MJ.
16. (a) 250 W/K. (b) 9.7·10^7 J/K. (c) 30 kW.
17.

CHAPTER 8

1. (a) 121 kW. (b) 73.5 kW. (c) 23.4 kNm.
2.
3. 2800 K.
4.
5. (a) Viscosity changes with temperature, and there is a current of substance due to evaporation. (b) dm/dt = – Im,pipe – Im,evaporation.
6.
7.
8. (a) 300 K, 6425 W/K. (b) 344.4 K, 6760 W/K. (c) 300 K, 9310 W/K.
9.

10.

CHAPTER 9

1. Minimum entropy production rate at a radius of 0.040 m.
2. Loss of energy from the pipe and pumping power do not add up to the loss of available power.
3.
4. (a) 2.174·10^6 W/K. (b) 815 MW. (c) 1.776·10^6 W/K, 5.33·10^8 W; yes.
5.
6. Add the additional heat exchanger surface at the cold end.
7. (a) ΠS = IE/TH – hA·(2 – TL/TH – TH/TL). (b) 482 K. (c) 514 K; two sinks for entropy at different temperatures.
8. (a) Balance of losses due to friction and to heat loss. (b) Dt_opt^2 = 1/T · RV · V^2 / (Ah) · T · Ta / (T – Ta)^2.
9.
10.

CHAPTER 10

1.
2.
3.
4.
5.
6.
7.
8. (1) γ = 1 + αV^2·c^2 / κP; (2) κT = 1/ρ · (αV^2/κP + 1/c^2); (3) ΛV = ρ · αV·c^2·κP / (κP + αV^2·c^2); where αV = – 1/ρ · ∂ρ/∂T is the temperature coefficient of expansion.
9.

CHAPTER 11

1. Both processes lead to source rate densities. In the case of production, the quantity appearing in a system is not coming from a different system.
2.
3. (a) $\partial\rho/\partial t - k \cdot \partial^2\rho/\partial x^2 = 0$. (b) $\partial^2\rho/\partial x^2 = 0$, ρ(x) = a + b·x, two boundary conditions are needed.
4.
5. (a) ∂ρf/∂t = πf(t,x), πf = net production – destruction rate,ρf = density of food.
6.
7. No; convection is implicity in the form using the material derivative.
8.
9. Gradient of a scalar function: grad(f) = (df/dx , df/dy); Divergence of a vector field: div(j) = djx/dx + djy/dy.
10. Coordinate independent form for a scalar function f: Df/Dt = df/dt + v·grad(f); v and grad(f) are vectors, the product is the scalar product.
11.
12.
13.

CHAPTER 12

1. (a) 2.0·10^7 W/(m^2·sr). (b) 5770 K; temperature of sunlight at the distance of the Earth is equal to the surface temperature of the Sun. (c) iEb = 3/4 · T · iSb; iSb = 4.6·10^3 W/(K·m^2·sr); 0.32 W/(K·m^2).
2. (b) Sun: 6.3·10^7 W/m^2; oven: 6.1·10^3 W/m^2.
3. F21 = A1/A2 · F12.
4. IE = σ/R_total · (T1^4 – T2^4); R_total = 958 1/m^2.
5. (a) κE = – 1/Δx · ΔiE / iE. (b) diE/dx = – μ·iE, where μ = κE + βE. (c) 3.5 · 10^(–5) 1/m.
6. l_mean = 0.06 m; κρ = 0.01 m^2/kg.
7. (a) y = 1/x^5 · 1/(exp(1/x) – 1). (b) 501 nm.
8. (a) 2330 K. (b) The new entropy of radiation is 2.7 times the old entropy.
9.
10.

CHAPTER 13

1. (a) 7.68·10^4 W/m^2. (b) 603 W. (c) 110 W/(K·m^3) and 206 W/(K·m^3). (d) 0.59 W/K.

2.

3. (a) Steeper at the colder end.

4. (a) 0.19 W/m^3. (b) 6.2·10^(–4) W/(K·m^3).

5. (b) dT/dx (L) = – sE/kE · L – 1/kE · jE(0). (c) – 0.025 K/m.

6.

7.

8. According to Equ.(13.54), the term in parentheses in Equ.(13.61) equals jS/kS.

9. (b) First two terms arise in thermal conduction alone; third term is due to dissipation in electric process.

10. dT/dx(cold) = 0; T(hot) = const.

11. (a) GE = const. (c) Power = a · IQ · (Th – Tc) – R · IQ^2; efficiency = Power / IE,th,h.

12.

CHAPTER 14

1.

2.

3.

4. Uniform model: includes entropy production due to mixing of incoming fluid stream with fluid present in the collector. This term does not occur in continuous models.

5.

6.

7.

8.

9.

10. Counter-flow: 0.833; parallel flow: 0.500.

11. Strongly unbalanced: e_unbalanced > e_balanced; nearly balanced: e_unbalanced ≈ e_balanced.

12.

13.

14.

15. Power = 4.4·10^12 W, efficiency ≈ 0.3.

16. Excess of gradient: 6.4·10^(–8) K/m, compared to actual gradient of 1.1·10^(–2) K/m.

CHAPTER 15

1. Moist air has smaller molar mass than dry air.

2.

3.

4. Use Equ.(15.37) – Equ.(15.39).

5. jnv,tot = – D/(R·Ta) · P/(P–Pv) · dPv/dz. (Remember: x = Pv/P.)

6. See Fig. 15.21 for a dynamical model that represents a similar situation.

7. (a) 1470 J/(K·kg) vs. 1550 J/(K·kg). (b) 2.24 MJ/kg; 1.8·10^9 W.

8.

9. 1 – T_out/T_in_av.

10. Efficiency increases if (1) boiler pressure is increased, (2) if condenser pressure is decreased. A condenser allows the pressure at the cold end to be decreased below atmospheric pressure.

11. 1 – 313/573 = 0.45 > 0.37 for the Rankine efficiency. Ideal Rankine cycle does not produce entropy, so the difference is not due to dissipation.

12.

13. (a) 0.15. (b) 19 m^2.

14.

15. (a) 6500 J/(K·kg), 3000 kJ/kg. (b) 190°C, 10 bar. (c) 1.0 bar, 0.9.

16. (a) – 53.26 kJ/K. (b) – 25.0 MJ. (c) 3.05 MJ.

CHAPTER 16

1. 1.79·10^9 W/(m^2·m).

2. 5800 K, 0.32 W/(K·m^2).

3.

4. See Problem 12 in Chapter 7, add a convective term A1·h_12·((T1 – T2) to the expression for IE from absorber to glass cover.

5.

6.

7. Pi_S_loss = 0.20 W/K, Pi_S_abs = 2.3 W/K for 1.0 m^2 of collector area.

APPENDIX 6

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