3 Thermal Physics

3.1 Nature of Science

Evidence through experimentation: Scientists from the 17th and 18th centuries were working without the knowledge of atomic structure and sometimes developed theories that were later found to be incorrect, such as phlogiston and perpetual motion capabilities. Our current understanding relies on statistical mechanics providing a basis for our use and understanding of energy transfer in science

3.1 Temperature & Energy changes

- **Thermal Equlibrium: Two objects placed in thermal contact will eventually come to the same temperature. When they do, we say they are in thermal equilibrium.**

- **The concept of absolute temperature scale allows us to define a third temperature scale – the absolute, or Kelvin, scale.**

The Kelvin Scale

- Absolute temperature is defined to be zero kelvin at absolute zero (temperature at which all matter has minimum kinetic energy) and 273.16 K at the triple point of water (unique temperature and pressure at which water can exist as liquid water, ice and water vapour)

- Therefore, the freezing point of water is 273.15 K, and the boiling point is 373.15 K.

$$T(K) = \theta(^oC) + 273$$

Internal Energy of a substance

- Internal energy of a substance is the total of the potential energy (arising from forces between molecules) and random kinetic energy of all the particles in the substance.

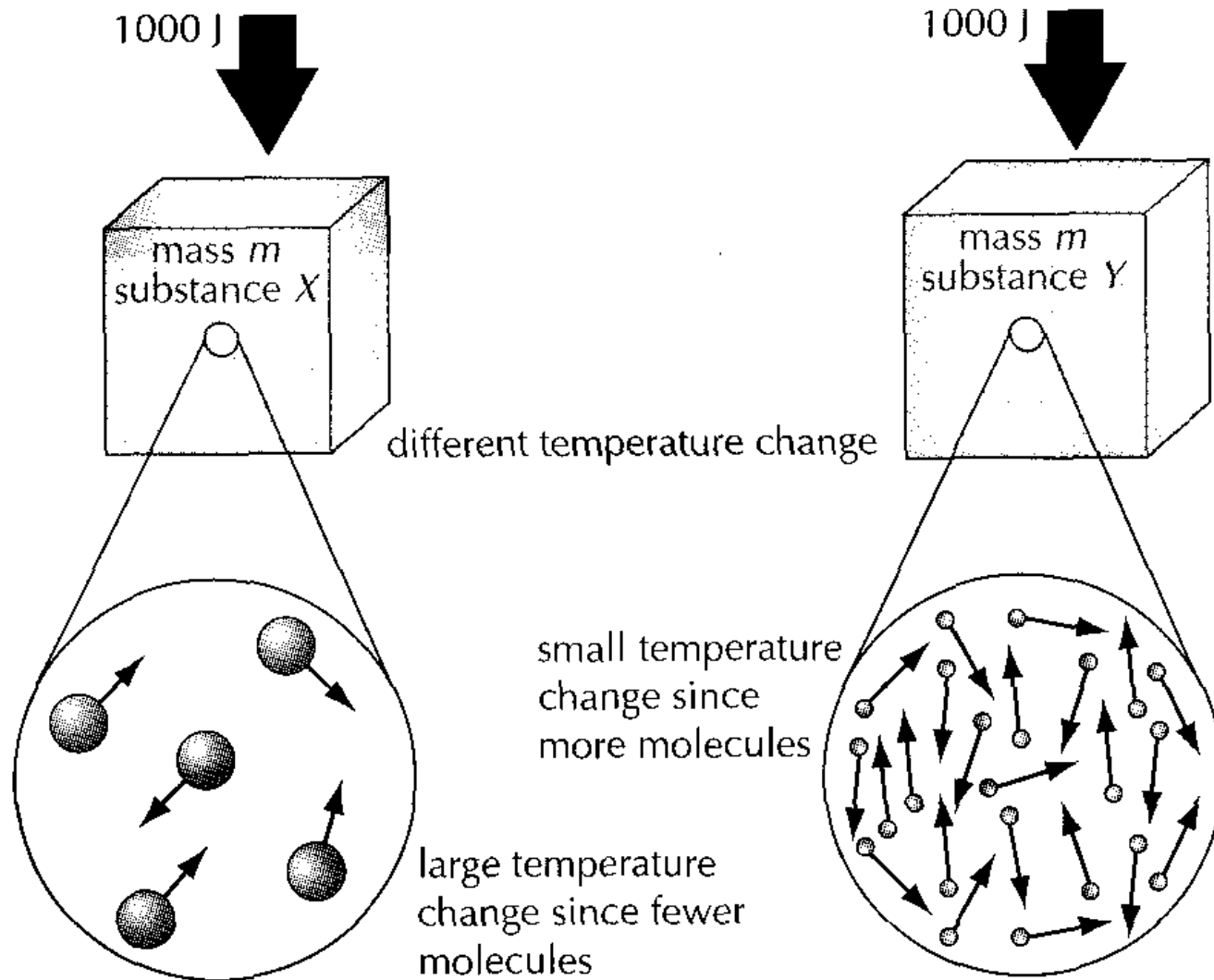- Internal Energy = Potential Energy + Kinetic Energy

Definitions

Specific heat capacity c is defined as the energy required to raise a unit mass of a substance by 1 K.

$$c = \frac{Q}{m\Delta T} \ (\text{J kg}^{-1} \ \text{K}^{-1})$$

Thermal capacity C of an object is defined as the energy required to raise its temperature by 1 K.

$$C = \frac{Q}{\Delta T} \ (\text{J K}^{-1})$$

1000 J

mass m
substance X

different temperature change

1000 J

mass m
substance Y

small temperature
change since
more molecules

large temperature
change since fewer
molecules

*Two different blocks with the same mass and same energy input
will have a different temperature change.*

Specific Heat Capacity

TABLE 14–1 Specific Heats
(at 1 atm constant pressure and 20°C unless otherwise stated)

Substance	Specific Heat, c kcal/kg·C° (= cal/g·C°)	J/kg·C°
Aluminum	0.22	900
Alcohol (ethyl)	0.58	2400
Copper	0.093	390
Glass	0.20	840
Iron or steel	0.11	450
Lead	0.031	130
Marble	0.21	860
Mercury	0.033	140
Silver	0.056	230
Wood	0.4	1700
Water		
Ice (−5°C)	0.50	2100
Liquid (15°C)	1.00	4186
Steam (110°C)	0.48	2010
Human body (average)	0.83	3470
Protein	0.4	1700

The amount of heat required to change the temperature of a material is proportional to the mass and to the temperature change:

$$Q = mc\,\Delta T$$

The specific heat capacity, _c_, is characteristic of the material. Some values are listed at left.

Estimating the specific heat capacity of a liquid

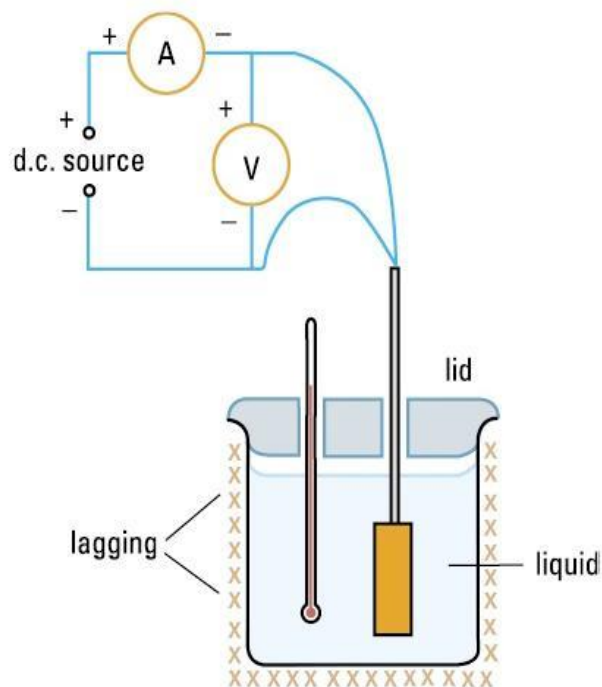▲Figure 11.6 Determination of specific heat capacity of a liquid

Objective

To determine the specific heat capacity of a liquid

Apparatus

copper calorimeter, heater, thermometer sensor, 12 V power supply, voltmeter, ammeter, data logger, mass balance

Procedure

1. Weigh the liquid and record the mass of liquid as m_ℓ.
2. Obtain the mass of the copper calorimeter m_c. (A copper calorimeter is a copper container and the specific heat capacity of copper c_c is 400 J kg^{-1} K^{-1}.)
3. Pour the liquid, whose specific heat capacity c_ℓ we want to determine, into the copper calorimeter.
4. Place the heater and the thermometer in the liquid. Ensure that the copper calorimeter is properly lagged (Figure 11.6).
5. Connect the temperature sensor to the data logger. Set the data logger to record temperature.
6. Start the recording of temperature. Note the initial temperature θ_i.
7. Switch on the power supply for t seconds (say 300 s).
8. After t seconds, switch off the heater. Continue recording the temperature for a while. Note the highest temperature θ_f reached.

Calculation

Power of the heater $= IV$

Then, thermal energy supplied by heater $Q = IVt$

The thermal energy absorbed by liquid $= m_\ell c_\ell (\Delta\theta)$

The thermal energy absorbed by copper calorimeter $= m_c c_c (\Delta\theta)$

We assume that all the thermal energy supplied is absorbed by the liquid and calorimeter because of no heat loss to the surroundings due to good lagging i.e.

$$\text{thermal energy supplied} = \begin{array}{c}\text{thermal energy} \\ \text{absorbed by liquid}\end{array} + \begin{array}{c}\text{thermal energy} \\ \text{absorbed by calorimeter}\end{array}$$

$$IVt = m_\ell c_\ell (\Delta\theta) + m_c c_c (\Delta\theta)$$

$$\therefore \quad c_\ell = \frac{IVt - m_c c_c (\theta_f - \theta_i)}{m_\ell (\theta_f - \theta_i)}$$

Moving particle theory

The moving particle theory uses models to explain the structure and nature of matter.

The basic assumptions of this moving particle theory relevant to thermal energy are:

-All matter is composed of extremely small particles

-All particles are in constant motion

-All collisions are elastic (Kinetic Energy conserved)

-A mutual attractive force exists between particles

Phases (states) of matter

Solids: Macroscopically, solids have a fixed volume and a fixed shape. This is because molecules are held together in position by bonds. However, the bonds are not absolutely rigid. The higher the temperature, the greater the vibrations.

Liquids: A liquid also has a fixed volume but its shape can change. The molecules are also vibrating, but they are not completely fixed in position. There are still strong forces between the molecules. This keeps the molecules close to one another, but they are free to move around each other.

Phases (states) of matter

Gas: A gas will always expand to fill the container in which it is put. The molecules are not fixed in position, and any forces between the molecules are very weak. This means that the molecules are essentially independent of one another, but they do occasionally collide.

Change of states
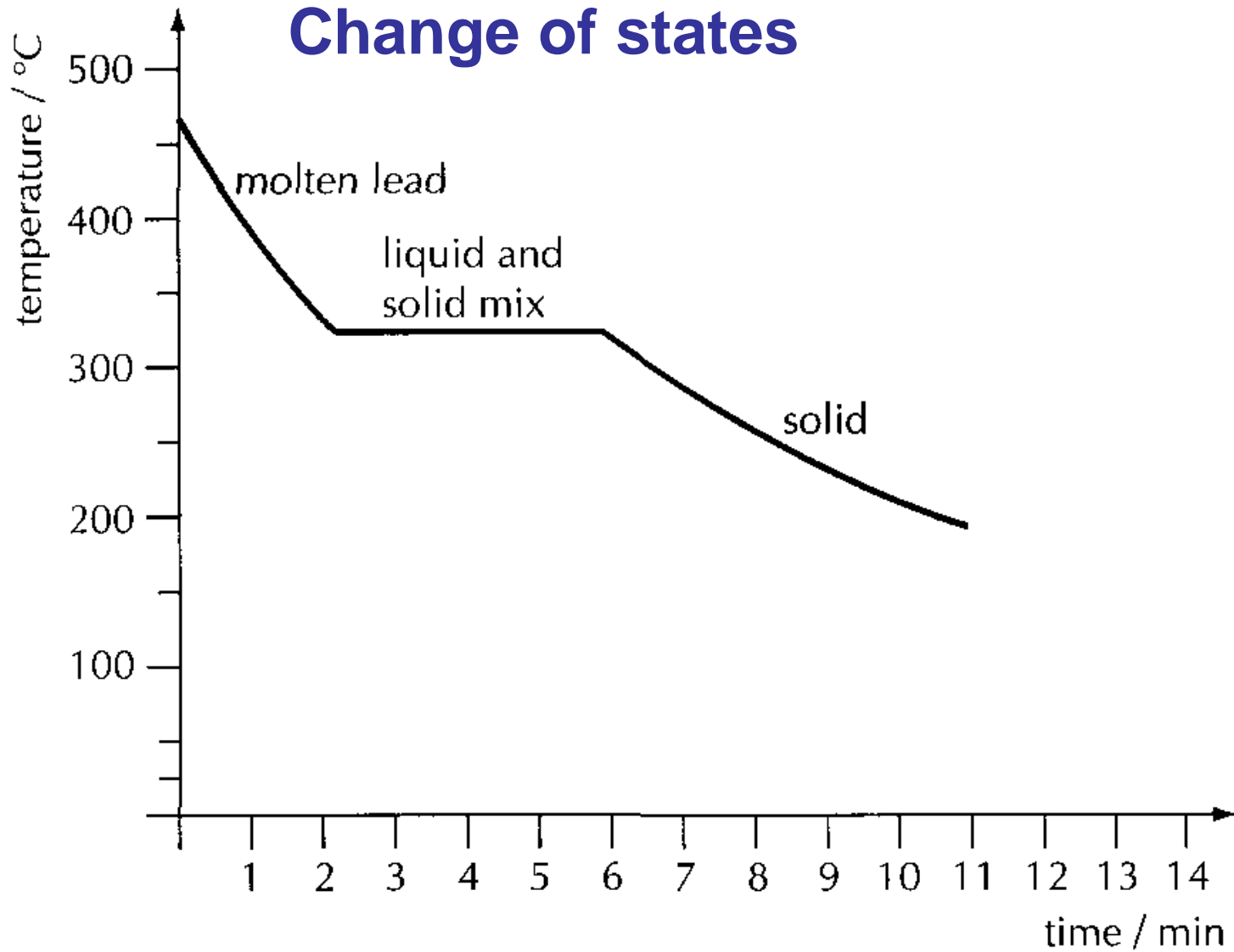
Cooling curve for molten lead (idealized)

Process of Phase Change in terms of molecular motion

When solid benzene is heated, the particles of the solid vibrate at an increasing rate as the temperature increases. Random kinetic energies of the molecules increase. There is no change in the molecular potential.

At the <u>melting</u> point, the particles vibrate with sufficient thermal energy to break from their fixed positions and begin to slip over each other. As the solid continues to melt, more and more particles gain sufficient energy to overcome the intermolecular forces. This goes on until the phase change is complete. The heat added during a change of state does not go to increasing the kinetic energy of individual molecules, but rather to break the close bonds between them so the next phase can occur. In this case, only the intermolecular potential energy of the molecules increases. The temperature always remains constant during a change of phase.

Process of Phase Change in terms of molecular motion

As heating continues, vibrational, rotational and translational kinetic energy is gained by the liquid molecules and therefore temperature increases. The intermolecular potential energy of the molecules stays constant during this time.

At the <u>boiling</u> point, the particles gain sufficient energy to overcome the inter-molecular forces present in the liquid to escape into the gaseous state. As before during a change of phase, only the intermolecular potential energy of the molecules increases. The temperature remains constant as before during a phase change. This process carries on until all liquid particles are changed into gas particles.

Further heating will result in higher temperature due to an increase in the kinetic energy of the gaseous molecules due to larger translational motion.

Process of Phase Change in terms of molecular motion

Gaseous molecules lose energy through thermal energy (heat) transfer by contact with another body at a lower temperature. If this loss is sufficient to lower the temperature of the gas molecules to its boiling point, then any further energy loss will result in a reduction of the molecular potential energy which then results in <u>condensation</u> and a change of state from gas to liquid.

Latent Heat

Energy is required for a material to change phase, even though its temperature is not changing. The thermal energy which a particle absorbs in melting or evaporating; or gives out in freezing or condensing is called the latent heat.
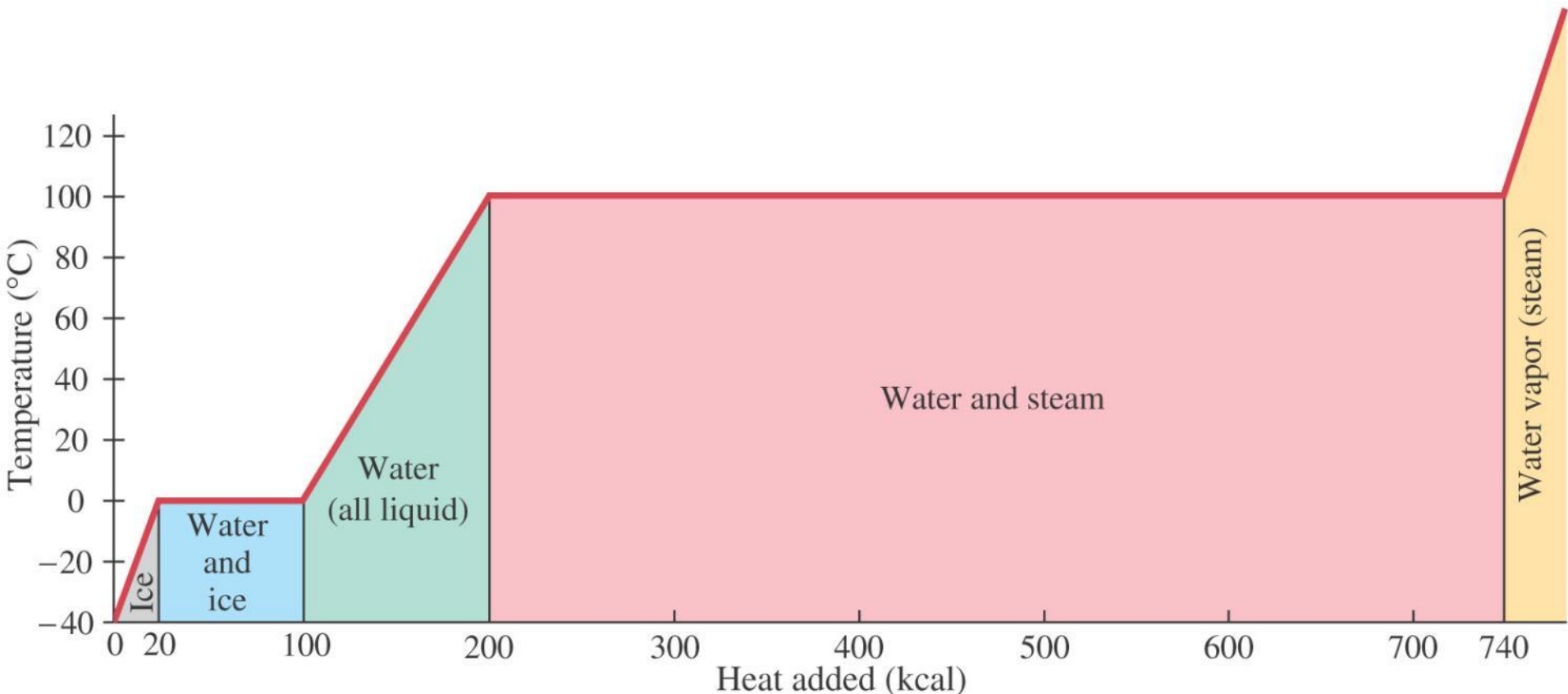
Specific latent heat

Specific latent heat **of a substance is defined as the amount of energy per unit mass absorbed or released during a change of phase.**

$$\text{Specific latent heat } \quad L = \frac{Q}{m} \quad (\text{J kg}^{-1})$$

Latent Heat

Specific latent heat of fusion, L_F: heat required to change unit mass of material from solid to liquid without a change in temperature.

Specific latent heat of vaporization, L_V: heat required to change unit mass of material from liquid to vapour without a change in temperature.

TABLE 14–3 Latent Heats (at 1 atm)

Substance	Melting Point (°C)	Heat of Fusion		Boiling Point (°C)	Heat of Vaporization	
		kcal/kg[†]	kJ/kg		kcal/kg[†]	kJ/kg
Oxygen	−218.8	3.3	14	−183	51	210
Nitrogen	−210.0	6.1	26	−195.8	48	200
Ethyl alcohol	−114	25	104	78	204	850
Ammonia	−77.8	8.0	33	−33.4	33	137
Water	0	79.7	333	100	539	2260
Lead	327	5.9	25	1750	208	870
Silver	961	21	88	2193	558	2300
Iron	1808	69.1	289	3023	1520	6340
Tungsten	3410	44	184	5900	1150	4800

[†] Numerical values in kcal/kg are the same in cal/g.

Worked Examples

1. How much heat input is needed to raise the temperature of an empty 20 kg vat made of iron from 10^0C to 90^oC ? (specific heat capacity of iron is 450 J(kg^{0}C)$^{-1}$)

   $Q = mc\Delta\theta = 20 \times 450 \times 80 = 720$ kJ

2. If 200 cm^3 of tea at 95^0C is poured into a 150 g glass cup initially at 25^0C, what will be the common final temperature of the tea and the cup when thermal equilibrium is reached, assuming no heat flows to the surroundings? (specific heat capacities of tea and glass are respectively 4186 and 840 J(kg^{0}C)$^{-1}$ and density of water is about 1 g cm^{-3})

   heat lost by tea = heat gained by cup

   0.20 kg x 4186 x (95 - θ) = 0.15 x 840 x (θ - 25)

   hence $\theta = 86^0$C

3. A 0.150 kg sample of a new metal alloy is heated to 540^0C. It is then quickly placed in 400 g of water at 10.0^0C, which is contained in a 200 g aluminium calorimeter cup. The final temperature of the system is 30.5^0C. Calculate the specific heat capacity of the new alloy. (c of water and aluminium are 4200 and 900, J(kg^{0}C)$^{-1}$). (500 J /kg^{0}C)

Worked Examples

1. How much energy does a freezer have to remove from 1.5 kg of water at 20^0C to make ice at -12^0C? (Specific latent heat of fusion of ice at 0^0C is 3.33×10^5 J kg^{-1} and specific heat capacity of water is 4200 J (kg^{0}C)$^{-1}$)

$Q = mc\Delta T + mL_f + mc_{ice}\Delta T$

$\quad = 1.5 \times 4200 \times 20 + 1.5 \times 3.33 \times 10^5 + 1.5 \times 2100 \times 12$

$\quad = 6.6 \times 10^5$ J

2. At a reception, a 0.50 kg chunk of ice at -10^0C is placed in a 3.0 kg of 'iced' tea at 20^0C. At what temperature and in what phase will the final mixture be? The tea can be considered as water. Ignore any heat flow to the surroundings, including the container. (specific heat capacity of ice is 2100 J (kg^{0}C)$^{-1}$)

heat gained by ice = heat lost by water

$(0.50 \times 2100 \times 10) + (0.50 \times 3.33 \times 10^5) + (0.50 \times 4200 \times \theta) = 3.0 \times 4200 \times (20 - \theta)$

Solving for $\theta = 5.0^0$C

All the mixture will consist of water.

3.2 Nature of Science

Collaboration: Scientists in the 19th century made valuable progress on the modern theories that form the basis of thermodynamics, making important links with other sciences, especially chemistry. The scientific method was in evidence with contrasting but complementary statements of some laws derived by different scientists. Empirical and theoretical thinking both have their place in science and this is evident in the comparison between the unattainable ideal gas and real gases

3.2 Modeling of a gas

The moving particle theory uses models to explain the structure and nature of matter.

When the moving particle theory is applied to gases, it is generally called the <u>kinetic theory of gases</u>. The kinetic theory relates the macroscopic behaviour of an ideal gas to the behaviour of its molecules.

The equation of state for an ideal gas is

$$pV = nRT$$

where n is the amount of gas in moles and $R = 8.31$ J K^{-1} mol^{-1} is the molar gas constant.

Assumptions of the kinetic model of an Ideal Gas

1. **Any gas consists of a large number of molecules.**

2. **The molecules of the gas are in rapid, random motion.**

3. **Collisions between the gas molecules are elastic.**

4. **Collisions between gas molecules and the walls of the container are also elastic.**

5. **There are no intermolecular attractive forces.**

6. **Intermolecular forces of repulsion act only during collisions between molecules; i.e. the duration of collisions is negligible compared with the time interval between collisions.**

7. **The volume of the gas molecules themselves is negligible compared with the volume of the container ;i.e. almost all the gas is empty space.**

Mole : The mole is the basic SI unit for "amount of substance". One mole of any substance is equal to the amount of that substance that contains the same number of atoms as 0.012 kg of carbon-12.

Molar mass : The mass of one mole of a substance is called the molar mass. If an element has a certain mass number, A, then the molar mass will be A grams.

Avogadro constant N_A: This is the number of atoms in 0.012 kg of carbon-12. It is 6.02 x 10^{23}.

Mass, Molar Mass and Moles

1 mol H_2 has a molar mass of 2 g

1 mol Ne has a molar mass of 20 g

1 mol CO_2 has a molar mass of 44 g

The number of moles in a certain mass of material:

$$n \ (mol) = \frac{mass \ (g)}{molar \ mass \ (g)}$$

$$n = \frac{N}{N_A}$$

Ideal Gas Law in Terms of Molecules: Avogadro's Number

Since the gas constant is universal, the number of molecules in one mole is the same for all gases. That number is called Avogadro's number:

$$N_A = 6.02 \times 10^{23}$$

The number of molecules in a gas is the number of moles times Avogadro's number:

$$N = nN_A$$

Examples

1. Estimate the mass of air in a room whose dimensions are 5 m x 3 m x 2.5 m high, at standard temperature and pressure (s.t.p.).

1 mol of any gas has a volume of 22.4 litres = 22.4 x 10^{-3} m^3

n = (5x3x2.5) / 22.4x10^{-3} = 1700 mol

Air is a mixture of about 20% oxygen and 80% nitrogen. The molecular masses are 2x16 u = 32 u and 2 x 14u = 28u, respectively, for an average of about 29u. Thus 1 mol of air has a mass of about 29 g = 0.029 kg.

so our room has a mass of air = 1700 x 0.029 = 50 kg

2. Use Avogadro's number to determine the mass of a hydrogen atom.

The mass of one atom equals the mass of 1 mol divided by the number of atoms in 1 mol, N_A.

One mole of hydrogen atoms has a mass of 1.008 x 10^{-3} kg and contains 6.02x10^{23} atoms.

Thus one atom has a mass of (1.008x10^{-3}) / (6.02x10^{23}) = 1.67x10^{-27} kg

Internal Energy of an ideal gas

Therefore, <u>internal energy is only dependent on temperature</u>:

Thus, in processes where only pressure and volume changes (with the temperature of the system maintained), there is no change in internal energy

Temperature and Pressure

Temperature is a measure of the average kinetic energy of the molecules in a substance.

The **pressure** of a gas is defined as the force exerted over an area.

$$\text{Pressure } P = \frac{F}{A} \quad (\text{N m}^{-2})$$

Kinetic Theory and the Molecular Interpretation of Pressure

The pressure of a gas is explained as follows:

-**When a molecule bounces off the walls of a container its momentum changes (due to the change in direction)**

-**There must have been a force on the molecule from the wall (Newton's second law)**

-**There must been an equal and opposite force on the wall from the molecule (Newton's third law)**

-**Each time there is a collision between a molecule and the wall, a force is exerted on the wall.**

-**The average of all the microscopic forces on the wall over a period of time means that there is effectively a constant force on the wall from the gas.**

-**This force per unit area of the wall is what we call pressure.**
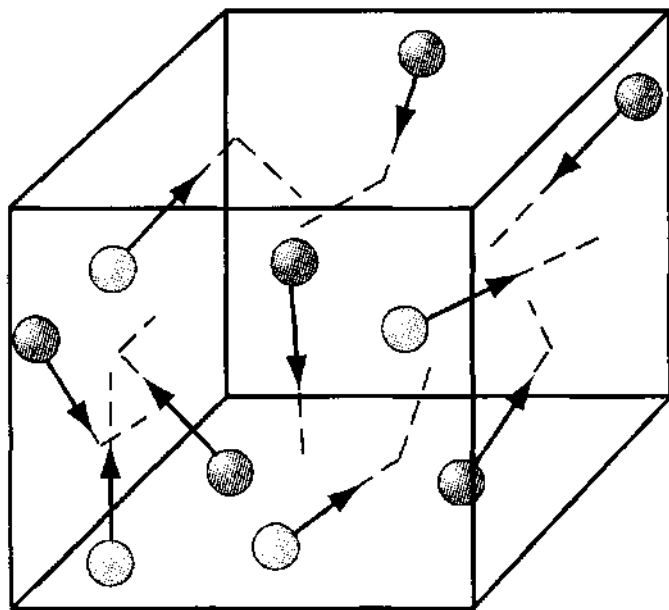
The pressure of a gas is a result of collisions between the molecules and the walls of the container.

before wall

after wall

result

overall force on molecule | overall force on wall
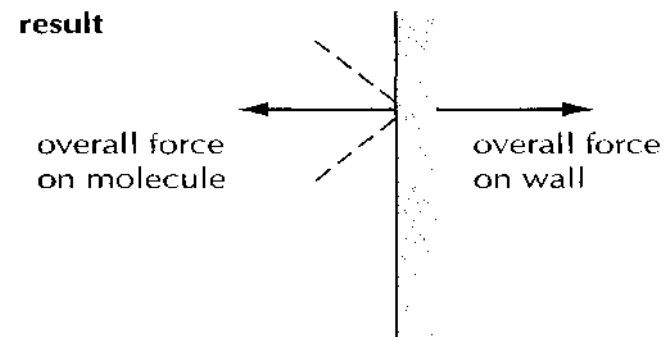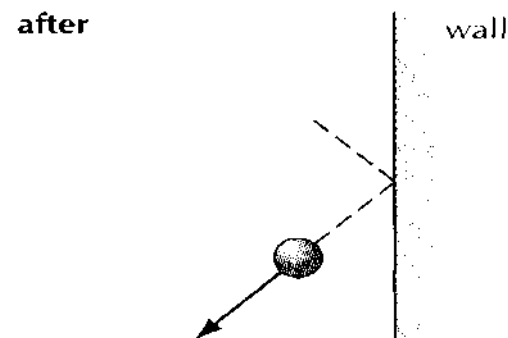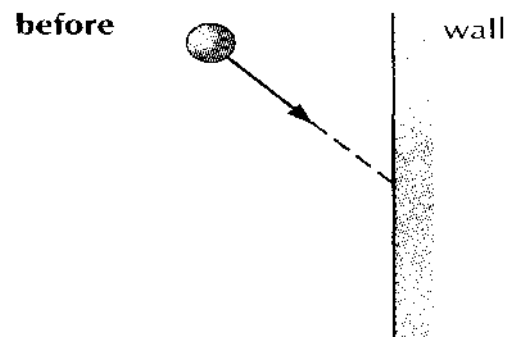
A single molecule hitting the walls of the container.

Kinetic Theory and the Molecular Interpretation of the Gas Laws

1. **Pressure law (P/T = constant at constant V)**

   If the temperature of a gas increases, the molecules have more average kinetic energy – they are moving faster on average. Fast moving molecules will have a greater change of momentum when they hit the walls of the container. Thus the microscopic force from each molecule will be greater. The molecules are moving faster so they hit the walls more often per second. For both these reasons, the total force on the wall increases. Thus the pressure also increases.

low temperature   high temperature
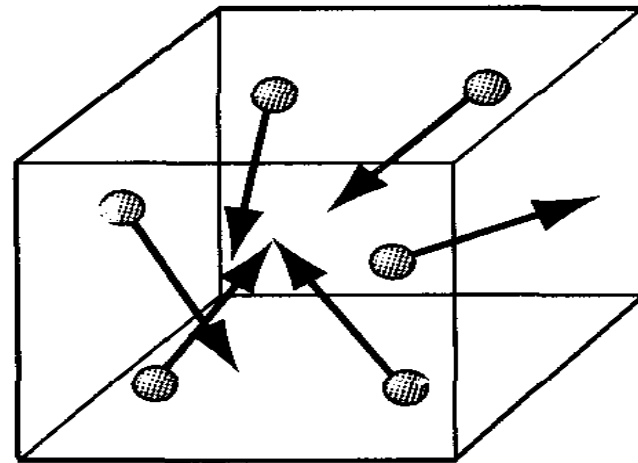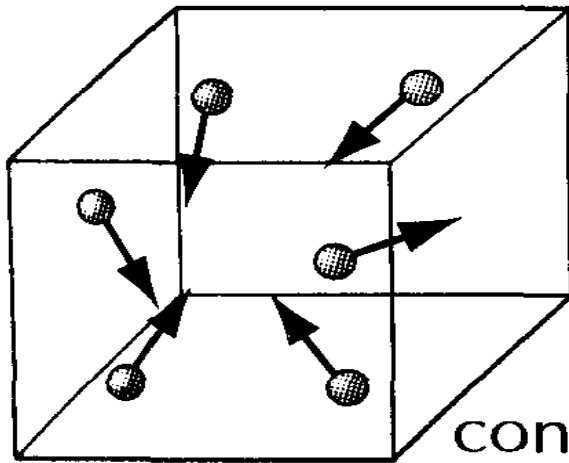
constant
volume

low pressure   high pressure

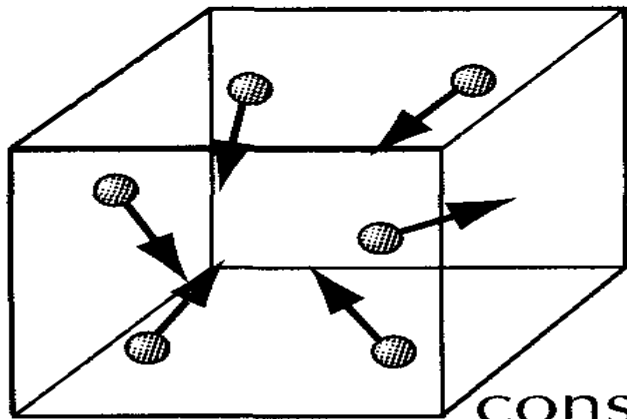*Microscopic justification of the pressure law*

Kinetic Theory and the Molecular Interpretation of the Gas Laws

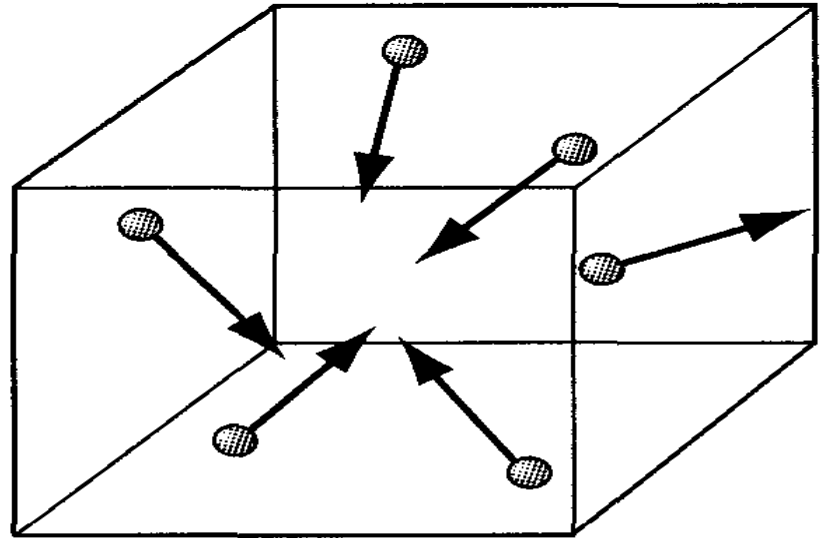**2. Charles' law (V/T = constant at constant P)**

A higher temperature means faster moving molecules. Faster moving molecules hit the walls with a greater microscopic force. If the volume of the gas increases, then the rate at which these collisions take place on a unit area of the wall must decrease. The average force on a unit area of the wall can thus be the same. Thus the pressure remains the same.

low temperature   high temperature

constant
pressure

low volume   high volume
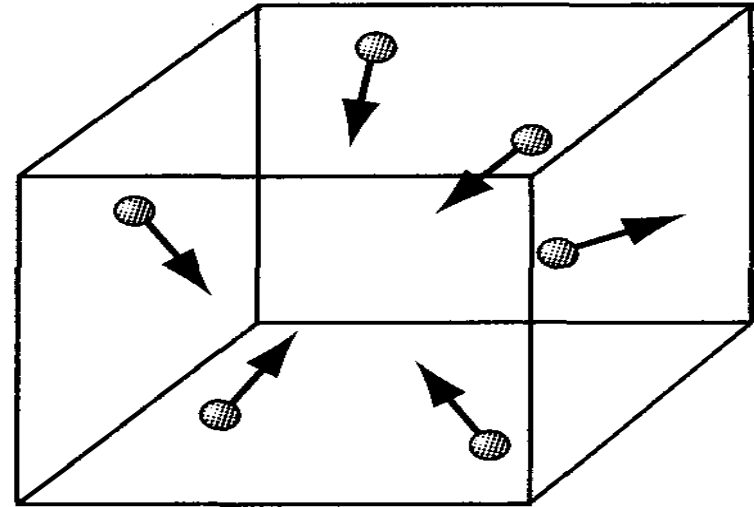
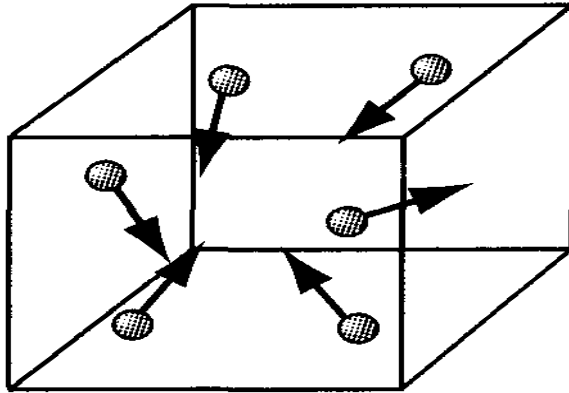*Microscopic justification of Charles's law*

Kinetic Theory and the Molecular Interpretation of the Gas Laws

3. Boyle's Law (pV = constant at constant T)

The constant temperature of gas means that the molecules have a constant average speed. The microscopic force that each molecule exerts on the wall will remain constant. Increasing the volume of the container decreases the rate with which the molecules hit the wall – average total force decreases. If the average total force decreases, the pressure decreases.

high pressure   low pressure

constant
temperature

low volume   high volume

Microscopic justification of Boyle's law

Kinetic Theory and the Molecular Interpretation of Pressure

- Since the pressure at a point in a fluid acts equally in all direction, the magnitude of pressure exerted on the wall by the gas can be written as

$$P = \frac{1}{3}\frac{Nm}{V}\overline{c^2} = \frac{1}{3}\rho\overline{c^2}$$

- Where P is the pressure of the gas, ρ is the total gas and $\overline{c^2}$ is the mean square speed of the molcules.

Kinetic Theory and the Molecular Interpretation of Temperature

The average translational kinetic energy of molecules in random motion in an ideal gas is directly proportional to the absolute temperature of the gas.

Kinetic energy of a gas molecule

$$\frac{1}{2}m < v^2 > = \frac{3}{2}k_B\text{T} = \frac{3}{2}\left(\frac{R}{N_A}\right)\text{T} \; ;$$

$k_B = 1.38 \times 10^{-23} \, JK^{-1}$ where m is the mass of gas molecule, <v²> is the mean square speed, k_B is the Boltzmann's constant, T is the absolute temperature, R is the Gas constant and N_A is the Avogadro's constant

Internal Energy of an ideal gas

Internal energy of an ideal (atomic) gas:

$$U = \frac{3}{2}nRT$$

$$U = \frac{3}{2}Nk_B T$$

Internal energy is defined as the sum of the potential energy and kinetic energy of the particles making up the system. But in an ideal gas, there are <u>no intermolecular forces</u>, so internal energy equals the kinetic energy of the particles. Therefore, any change in the temperature of the gas will result in a change in the internal energy of the gas.

Internal energy is only dependent on the temperature of the system for a fixed mass of ideal gas.

Differences between Real and Ideal Gases

Internal energy is defined as the sum of the potential energy and kinetic energy of the particles making up the system. In a real gas, there would be some intermolecular forces. So internal energy of a real gas would be made up of both potential and kinetic energy.

In order for real gases to approximate that of ideal gases, the real gases would need to satisfy the requirement of

- Low Pressure

- Moderate Temperature

- Low Density