Energy Flow and Living Cycles

The Probability of Life

The chemical constituents of a typical living cell, say, an *E. coli* bacterium, are known in considerable detail. The major elements are carbon, hydrogen, nitrogen, oxygen, phosphorous and sulphur, in that order, or CHNOPS for short, making a sound like a cow munching on fresh, green grass. These go to make up the organic polymers such as proteins, nucleic acids, membrane lipids, carbohydrates, and small molecular weight cofactors and intermediates of metabolism. A question of great interest to scientists is: how probable is life in its simplest form of the cell? The problem can be considered as follows. Suppose one were to mix together the chemical elements in their appropriate amounts and proportions in each of an infinite array of sealed containers kept indefinitely in a very big water bath (or reservoir) at 300°C, say, what fraction of them would eventually develop into living cells? The answer is $10^{-10^{11}}$, an infinitesimally small number, so small that there has not been time, nor matter enough in the whole of the universe for it to happen even once. How is such a number arrived at? Is there any basis for this kind of estimate?

The (hypothetically) infinite array of systems with the same chemical composition, volume and temperature, is a 'canonical ensemble', in the language of statistical mechanics, which is allowed

to go to equilibrium. The theory is that eventually, *every* possible configuration of the atoms or microstates, *i*, with corresponding energy level, e_i, will be explored, some of which would correspond to those in the living system. But because the energy level of the living state is so much higher than the average in the equilibrium ensemble, the probability of those states occurring is vanishingly small.

The living cell has a very large amount of energy stored in covalent bonds as electronic bond energies, considerably more than the thermal energies that exist in the equilibrium state. So large, in fact, that the probability of getting there by chance fluctuation around the equilibrium state is essentially nil. So how come there are living organisms at all? The immediate answer is energy flow. Energy flow greatly increases the probability for life, and is absolutely essential for its maintenance and organisation. These are some of the insights offered in the wonderful book, *Energy Flow in Biology*[1] by biophysicist Harold Morowitz now Science Board Chair Emeritus at the Sante Fe Institute in the United States. We shall explore some of his ideas in the pages following.

Energy Flow and Material Cycles

The concept of energy flow in biology is familiar to every bio-chemist and ecologist. It is the energy from sunlight, trapped by green plants, which flows through the whole biosphere, beginning with herbivores and insects which feed directly on green plants, through to other 'trophic layers' of animals that in turn feed upon them. At every stage, the energy is further transformed, rearranged and degraded, and a fraction lost as heat. Accompanying the energy flow is a *cycling* of materials through the biosphere: carbon dioxide, water, nitrogen, sulphates and phosphates are 'fixed' by green plants and bacteria into high electronic energy compounds, which are incorporated or pass through the bodies of animals in the biosphere before they are broken down and returned to the soil and the atmosphere for general recycling. (Cycling and re-cycling are indeed
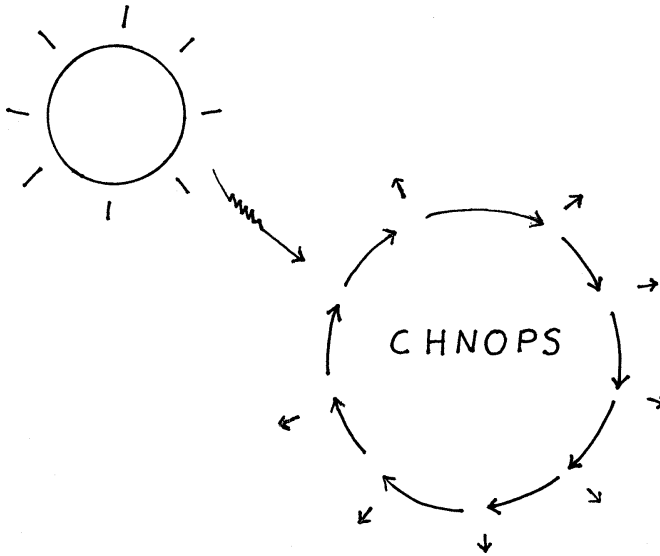
Figure 4.1 The CHNOPS cycle and energy flow.

nature's way.) The relationship between energy flow and the cycling of the elements in the biosphere is represented very schematically in Fig. 4.1. The 'cycle' is actually a lot more complicated. It is a composite of many parallel cycles and epicycles variously connected, and branching at different points.

This intimate relationship between energy flow and the cycling of the elements turns out not to be at all fortuitous. For it is the energy flow that organises the material system, taking it far away from thermodynamic equilibrium by raising its energy level, producing gradients, and cyclic flow patterns of materials (and energy), in short, generating a hierarchy of space-time structures, which in turn organises the energy flow. The key to life is in this mutuality of spontaneous relationship between the system and the environment, each in turn the organiser and the organised (Fig. 4.2).

The same space-time catenation of processes occurs on the ecological level as in individual organisms, involving larger dimensions and longer durations, of course. Ecological processes are continuous
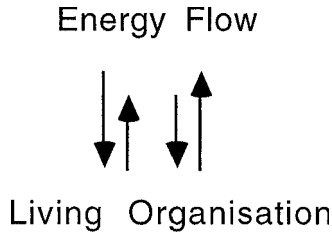
Energy Flow

Living Organisation

Figure 4.2 Energy flow and living organisation.

with, and impinge upon individual processes in living organisms, and subject to similar cybernetic principles of regulation; so much so that James Lovelock, who calls himself a 'geophysiologist' has proposed that the earth is like a superorganism.[2] And hence, a lot could be learned by concentrating on the global homeostatic, feedback mechanisms that account for the stability of the earth's ecological system as a whole. Many other scientists, including US chemist Sidney Fox, who worked on the origin of life and produced the first proteinoid protocells,[3] also believed that biological evolution is continuous with the evolution of the solar system and chemical evolution, and by no means the result of a series of lucky 'frozen accident'.[4]

These fascinating aspects are beyond the scope of the present book, but they do emphasise the continuity between the living and non-living, which *is* my thesis. Without further ado, let us go on to consider Morowitz's idea that energy flow leads to space-time structures, in particular, to cycles.

## Dynamic Molecular Order from Energy Flow

Some simple examples suffice to illustrate how molecular order can arise from energy flow. Figure 4.3 is a model system consisting of a chamber containing an ideal gas (i.e., at low enough concentrations such that the volume of individual molecules do not matter, and the individual molecules do not interfere much with one another). The left side is kept indefinitely at temperature T_1 by contact with
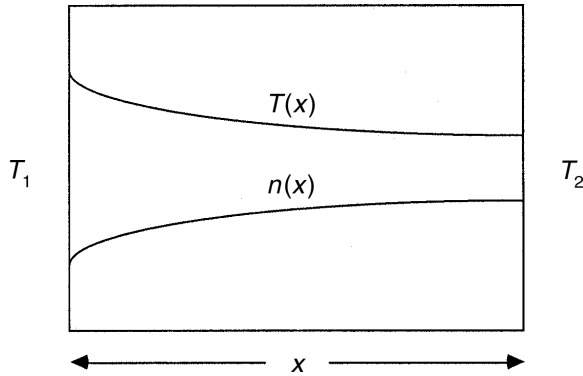
Figure 4.3 Heat flow and the formation of a concentration gradient in a volume of ideal gas.

a large reservoir at the same temperature, and the right side kept by contact with an equally large reservoir at temperature T_2; with $T_1 > T_2$. A steady flow of heat is therefore maintained across the chamber from left to right, or from 'source' to 'sink'.

The result is a temperature gradient from left to right, and at the same time, a gradient in the concentration of the molecules, increasing from the 'hot' end to the 'cold' end. This has been theoretically predicted and experimentally observed. The calculations are quite complicated, but it is intuitively easy to see how the concentration gradient arises. The hotter molecules at the left have more kinetic energy (which is proportional to kT, see p. 19); therefore, they tend to have higher velocities than those on the right, and there is a net (convectional) movement of molecules towards the right where they cool down and lose kinetic energy. At steady state, this is balanced by diffusion from the right back to the left.[5] This would go on indefinitely as long as the temperature difference is maintained. This is the simplest version of a 'dissipative structure'[6] that must be maintained by a continuous flow and dissipation of energy. If the chamber is 'adiabatically' isolated from the reservoirs, i.e., isolated so that there is no heat exchange with the reservoirs, it would soon decay back to uniform equilibrium in which the temperature and concentration everywhere will be the same.

$$T_2$$

$$T_1$$
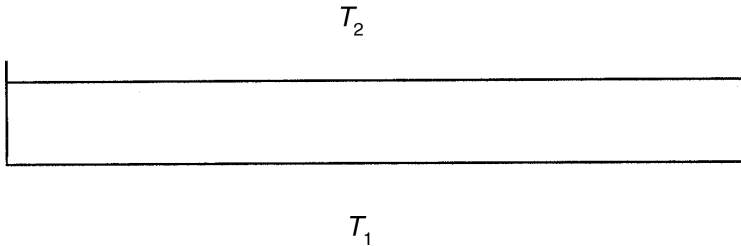
Figure 4.4 Heat flow in a shallow pan of water.

The next example involves the formation of more complicated structures. A shallow pan of water is heated uniformly from below (Fig. 4.4). For a small temperature difference, the situation is similar to the previous example: a temperature gradient is maintained across the depth of the water from the bottom to the top, and a density gradient in the opposite direction. The one difference here is that the heat transfer will occur by conduction rather than convection, for the water molecules themselves do not alter their mean position in the process.

If we increase the temperature difference, a critical value will be reached at which bulk movements will occur in the liquid. A series of regular, convection cells are formed, giving a honeycomb appearance when viewed from above (Fig. 4.5). These so-called Bénard convection cells (or more accurately, Bénard Rayleigh cells[7]) arise as the low density, lighter water at the bottom of the pan repeatedly rises to the top while the denser water at the top sinks to the bottom, and so on in a cyclic manner. As convectional movements begin in different parts of the pan and increase in magnitude, the system would soon end up in a situation where all the convection cells are of the same size and are cycling together, as that is the most stable dynamical state.

Let us dwell on this remarkable state in terms of what is happening at the molecular level. Each cell involves the concerted cyclical movement of some 10^{23} individual water molecules (as schematically represented in Fig. 4.6). Furthermore, all the cells in the pan are
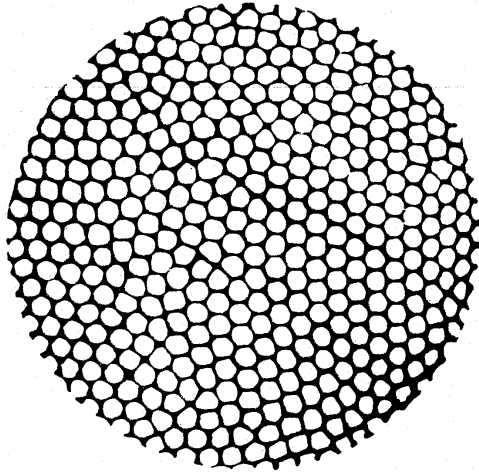
Figure 4.5 The Bénard-Rayleigh convection cells.[8]

synchronised with respect to one another. In technical language, *a non-equilibrium phase transition to macroscopic order has taken place.* Before phase transition, the individual water molecules move around randomly and aimlessly without any order or pattern. At phase transition, however, they begin to move collectively until all at once, the molecules are dancing together in cellular formations as though choreographed to do so. Like the previous example, the convection cells are dissipative structures dependent on the flow of energy for their continued existence. It is appropriate also to refer to them as 'coherent structures' dynamically maintained. Do keep in mind this wonderfully evocative picture of global order constituted of micro-scopically coherent motions when we try to imagine what happens in a living system later on.

In both examples of non-equilibrium structures just described, there is a net cycling of molecules around the system, from the hot end to the cold end and back again, the situation being more visually dramatic in the second case. What happens when chemical reactions are involved? Does chemical cycling also take place as the result of energy flow?
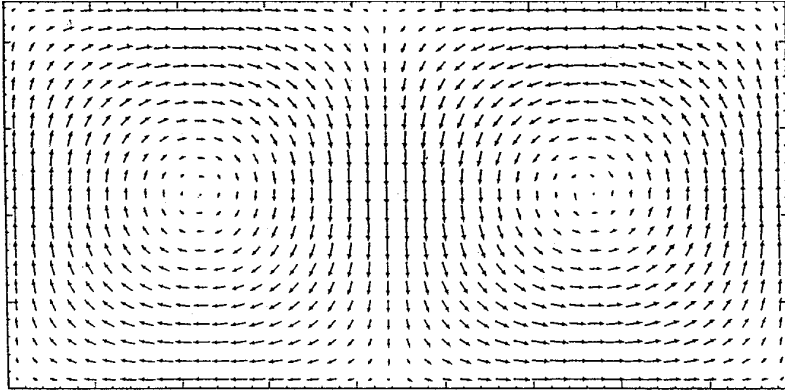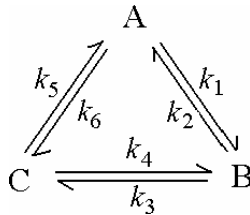
Figure 4.6 Coherent molecular motions in the convection cells.[9]

A Theorem of Chemical Cycles

Consider a reactor maintained by contact with a large reservoir at temperature T, in which are three chemical species, A, B, and C, reacting according to the following scheme:[10]

where the k's are the rate constants: the odd numbered ones refer to rates in the forward direction — A to B to C, and the even numbered ones in the reverse direction. At equilibrium, i.e., without energy flow, forward and backward reactions are equal. This is *the principle of microscopic reversibility* or *detailed balance*, which is considered of great importance in chemistry. Hence,

$$k_1[A] = k_2[B]$$
$$k_3[B] = k_4[C] \tag{4.1}$$
$$k_5[C] = k_6[A]$$

The bracketed letters represent concentrations of the respective chemical species. Thus, at equilibrium, there is no net flow around the system, as the forward and backward reactions are occurring at the same rate and are therefore in *detailed balance* at every step. Under the additional constraint that the total amount of material in the reactor is constant, i.e.,

$$[A]+[B]+[C]=M \tag{4.2}$$

one can solve for the equilibrium concentrations of each species. These are,

$$[A]_{eq} = k_2 k_4 M/k'$$
$$[B]_{eq} = k_1 k_4 M/k' \tag{4.3}$$
$$[C]_{eq} = k_1 k_3 M/k'$$

where $k' = k_2 k_4 + k_1 k_4 + k_1 k_3$.

If energy now flows into the system so that a steady state is maintained with a net flow of material around the system from A to B to C, the principle of microscopic reversibility will no longer hold: there will not be a detailed balance in every step. In the three species system,

$$k_1[A]>k_2[B]$$
$$k_3[B]>k_4[C] \tag{4.4}$$
$$k_5[C]>k_6[A]$$

In other words, the material must cycle around the system. The flow, or rate at which the material is cycling around the system is given by,

$$F = k_1[A]-k_2[B]= k_3[B]-k_4[C]= k_5[C]-k_6[A] \tag{4.5}$$

This result can be restated in a formal, general way. A canonical ensemble of systems is at equilibrium with i possible states, where f_i is the fraction of systems in state i (also referred to as occupation

numbers of the state i), and t_{ij} is the transition probability that a system in state i will change to state j in unit time. The principle of microscopic reversibility requires that every forward transition is balanced in detail by its reverse transition, i.e.,

$$f_i t_{ij} = f_j t_{ji} \qquad (4.6)$$

If the equilibrium system is now irradiated by a constant flux of electromagnetic radiation such that there is net absorption of photons by the system, a steady state will be reached at which there is a flow of heat out into the reservoir (sink) equal to the flux of electromagnetic energy into the system. At this point, there will be a different set of occupation numbers and transition probabilities, f_i' and t_{ij}' for there are now both radiation induced transitions as well as the random thermally induced transitions characteristic of the previous equilibrium state. This means that for some pairs of states i and j,

$$f_i' t_{ij}' \neq f_j' t_{ji}' \qquad (4.7)$$

For, if the equality holds in all pairs of states, it must imply that for every transition involving the absorption of photons, a reverse transition will take place involving the radiation of the photon such that there is no net absorption of electromagnetic radiation by the system. This contradicts our original assumption that there is absorption of radiant energy (see previous paragraph), so we must conclude that the equality of forward and reverse transitions does not hold for some pairs of states.

However, at steady state, the occupation numbers (or the concentrations of chemical species) are time independent (i.e., they remain constant), which means that the *sum* of all forward transitions equals to the *sum* of all backward transitions, i.e.,

$$df_i'/dt = 0 = \sum (f_j' t_{ji}' - f_j' t_{ji}') \qquad (4.8)$$

But it has already been established that some $f_j' t_{ji}' - f_j' t_{ji}'$ are non-zero. That means other pairs must also be non-zero to compensate. In

other words, members of the ensemble must leave some states by one path and return by other paths, which constitutes a cycle.

The above line of reasoning led Morowitz to an important theorem:

> *In steady state systems, the flow of energy through the system from a source to a sink will lead to at least one cycle in the system.*
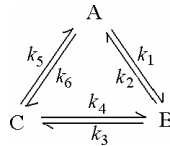
The formation of steady state cycles has the important thermo-dynamic consequence that, despite large fluxes of materials and chemical transformations in the system, the net change in entropy of the *system* is zero, because entropy is a state function (as mentioned in Chapter 2), a return to the same state will always entail no net entropy change. Of course, the compensatory change in entropy of the surroundings could be greater than zero, but entropy does not *accumulate* in the system, provided that the cycles are perfect in the sense that *exactly* the same state is reproduced, which is definitely not the case in real life. But the steady state approximation leads to some quite remarkable consequences, as I shall describe in a later chapter.

More mathematical treatments of the consequences of energy flow may be found in the writings of Belgian Nobel Laureate Chemist Ilya Prigogine and his colleagues,[11] who showed how dissipative structures can arise in systems far from thermodynamic equilibrium based on the analysis of entropy production. Theoretical physicist Hermann Haken at the University of Stuttgart in Germany, taking a different approach, identifies 'order parameters' as macroscopic descriptors of cooperative phenomena in systems far from equilib-rium, which include the Bénard-Rayleigh convection cells we have just seen, as well as lasers (Chapter 9) [12] In such instances, random energy fed into the system will nevertheless lead to macroscopic organisation as the system passes from the thermodynamic regime of random microscopic motion of many degrees of freedom to a *dynamic* regime that has only one, or a few degrees of freedom. This is also to be expected of a system in which all the processes are linked, or *coupled* together in a symmetrical way.[13] Let us explore further what that means.
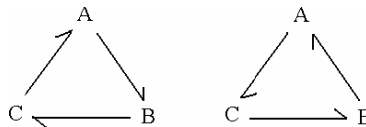
Coupled Cycles and the Steady State

Norwegian-American physical chemist Lars Onsager used the same principle of microscopic reversibility (p. 45) to derive another significant result in non-equilibrium thermodynamics — the *Onsager reciprocity relation* — that shows how symmetrical coupling of processes can arise naturally in a system under energy flow.[14]

The principle of microscopic reversibility can be expressed as follows: under equilibrium conditions, any molecular process and its reverse will be taking place on the average at the same rate. As we have seen in the previous section, it implies that equilibrium is never maintained in a cyclic process *at the molecular level*. To return to the three species system (p. 45), the principle of microscopic reversibility, as conventionally interpreted by chemists, requires that the balance be maintained at every step:

$$
\begin{array}{c}
A \\
{}_{k_5}\diagup\diagup \quad \diagdown\diagdown {}^{k_1} \\
{}_{k_6} \qquad\qquad {}^{k_2} \\
C \underset{k_3}{\overset{k_4}{\rightleftharpoons}} B
\end{array}
$$

However, as in the derivation of Morowitz's theorem, the interconversions could be legitimately considered as occurring in a forward sequence, A → B → C → A, linked or coupled to a backward sequence, C → B → A → C, so that they balance each other *on the whole*, i.e.,

$$
\begin{array}{cc}
A & \qquad\qquad A \\
\diagup\ \ \diagdown & \qquad\quad \diagup\ \ \diagup \\
C \longleftarrow B & \qquad C \longrightarrow B
\end{array}
$$

It turns out that the rate equations (which are like those on p. 46, and I shall not write down again here) have the same form, whether one assumes detailed balance at every step or merely overall balance. In other words, *detailed molecular balance at every step is not required even for thermodynamic equilibrium*. (This is what I had in mind when

I drew your attention to the subtlety of the concept of thermodynamic equilibrium in the previous chapter.) So a system in equilibrium may nevertheless have within it *balanced flows* of energy and material, as long as the flows are linearly proportional to the forces. This is not surprising in retrospect, as the laws of thermodynamics were themselves a generalisation of macroscopic phenomena, and do not depend on the knowledge of what is happening in detail at the molecular level.

What this means is that many *locally* non-equilibrium situations involving cyclic flow processes can be described as near approximations to the equilibrium situation, more specifically, as *fluctuations* occurring within a larger, encompassing equilibrium system, so long as the flows and forces which tend to restore the equilibrium are linearly proportional to one another.

We have come across such situations already. In the example on heat flow in a volume of an ideal gas (p. 43), a steady state is arrived at in which the convectional flow of hot molecules to the right is balanced by the diffusion of cooler molecules back to the left. So the transport of energy from left to right is linked or coupled to the diffusion of molecules from right to left to maintain a concentration gradient. In the case of heat flow in a pan of water (Fig. 4.4), we have two different 'steady states' depending on the temperature difference, only the first of which — at small temperature differences — can be regarded as an approximation to equilibrium: the flow of heat by conduction from the bottom to the top is coupled to the maintenance of a density gradient in the reverse direction. Many other non-equilibrium processes may be approximated in this way. The flow of electrons across a biological membrane, for example, can couple linearly to the diffusion of inorganic ions.

Onsager set out to describe by means of general 'thermodynamic equations of motion', the rates of processes such as energy flow and diffusion, which are assumed to be linearly proportional to the 'thermodynamic forces' generating them. These forces are just the gradients of temperature, or of chemical/electrical potentials, which may be seen to be the causes of the flows.

Let $\mathbf{J}_1$ and $\mathbf{J}_2$ represent two coupled flow processes, and $\mathbf{X}_1$, $\mathbf{X}_2$, the corresponding forces, then,

$$\mathbf{J}_1 = L_{11}\mathbf{X}_1 + L_{12}\mathbf{X}_2$$
$$\mathbf{J}_2 = L_{21}\mathbf{X}_1 + L_{22}\mathbf{X}_2$$

(4.9)

The coefficients L_{11} and L_{22} are proportionality constants relating the flows each to their respective force. L_{12} and L_{21} are the cross coefficients representing the extent to which coupling occurs: in other words, how the force of one process influences the flow of the other process. For example, the two flows could be electricity and inorganic ions, due respectively to an electric potential gradient and an ionic concentration gradient. The cross-coefficients tell us the extent to which the electric potential gradient influences the diffusion of ions, and conversely, how the ionic concentration gradient affects the flow of electricity.

Onsager then showed that if the principle of microscopic reversibility is true for a system in equilibrium and near equilibrium, it implies that,

$$L_{12} = L_{21}$$

(4.10)

This means that the coupling of the two processes becomes completely symmetric, even in states of non-equilibrium at the molecular level. In other words, the force of each process has the same *reciprocal* effect on the other process. This result can be generalised to a system of many coupled processes described by a set of linear equations of the same form as Eq. (4.9),

$$\mathbf{J}_i = \sum_k L_{ik}\mathbf{X}_k$$

(4.11)

$\mathbf{J}_i$ is the flow of the ith process (i = 1, 2, 3 … n), $\mathbf{X}_k$ is the kth thermodynamic force (k = 1, 2, 3, … n), and Lik are the proportionality coefficients (where $i = k$) and coupling coefficients (where $i \neq k$). It may happen that some of the coupling coefficients are zero (in cases where the processes do not interact at all). Some may be positive while others are negative. Still, for such a multi-component system,

certain of the couplings will be symmetrical; in other words, for *some i* and *k* (*i* ≠ *k*),

$$L_{ik} = L_{ki} \tag{4.12}$$

The mathematical entities of the Onsager's thermodynamic equations of motion [Eq. (4.11)] can all be experimentally measured and verified, although it has not yet been systematically applied to the living system.[15] Nevertheless, as we shall see, it captures a characteristic property of living systems: the reciprocal coupling of many energetically efficient processes. This raises once again the interesting question as to whether most of the processes in the living system may be operating near to local equilibrium.

As we have seen in the previous chapter, the intricate space-time differentiation of the organism specifically allows for the establishment of a hierarchy of local near-equilibrium regimes, even though the organism as a whole is a system far from equilibrium. Perhaps one of the *raisons d'etre* of development is to set up the nested hierarchies of space-time domains where local equilibrium can be maintained in a macroscopically *non*-equilibrium system. Thus, paying attention to space-time structure leads us to a much more subtle view of both equilibrium and non-equilibrium. A system in equilibrium can have local non-equilibrium regimes; conversely, a system in non-equilibrium can also possess domains in local equilibrium.

Another intriguing question is, what sort of couplings of processes can arise far from thermodynamic equilibrium? In the system of Bénard-Rayleigh convection cells, for example, the flow of heat is obviously coupled to the convectional movement of molecules, although the flows and forces are not linearly related in such systems far from equilibrium, which include the Beloussov-Zhabotinsky reaction (Chapter 3). Nevertheless, these 'dissipative structures' arise in such a regular, predictable way that one cannot help wondering whether a general, or 'canonical' mathematical relationship concerning the coupling of processes far from equilibrium is hovering in the wings, awaiting discovery by some mathematically able physical chemists.[16]

There is, indeed, already a *balance theorem* due to Indian-born Nobel Laureate physicist Subramanyan Chandresekhar,[17] which states that instability of the linear steady state of the Bénard-Rayleigh problem (where the flow of heat by conduction exactly counteracts the density gradient) occurs at the minimum (critical) temperature gradient at which a balance can be steadily maintained between the kinetic energy dissipated by viscosity and the internal energy released by the buoyancy force. Similarly, Glansdorff and Prigogine[18] state that the Bénard-Rayleigh instability occurs at the minimum temperature gradient at which a balance can be steadily maintained between the entropy generated through heat conduction by the temperature fluctuations and the corresponding entropy flow 'carried away' by the velocity fluctuations. These are deep problems to which we shall return in Chapter 6.

The Many-Fold Coupled Cycles of Life

Based on the above insights, we can *begin* to understand two main aspects of the living system: the ubiquitous cycling that occurs at every level of living organisation, and the coupling of all the cyclic processes. This is so from the ecological cycle of the biosphere to the biochemical metabolic cycles in organisms down to the whirring of molecular machines, all meticulously choreographed, like the molecules in the Bénard Rayleigh convection cells, to spin and turn at different rates, each in step with the whole.

The biochemical outline of the ecological cycle is very simple. The photons absorbed by green plants split water molecules and reduce carbon dioxide, resulting in the formation of carbohydrates and oxygen. In respiration, the converse takes place: carbohydrates are oxidised to restore carbon dioxide and water:
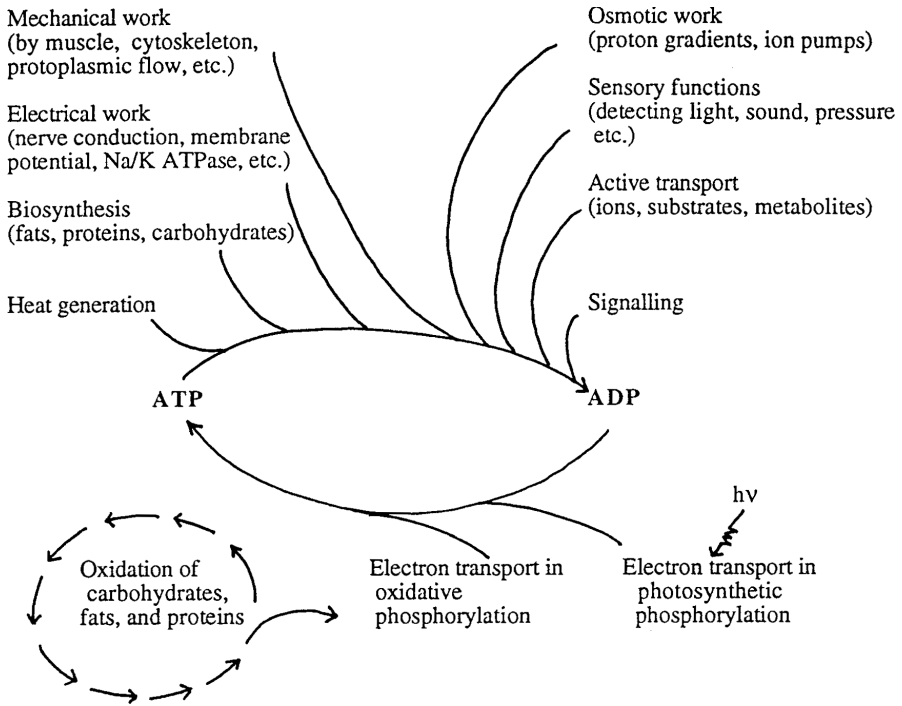
$$H_2O + CO_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} \text{carbohydrates} + O_2$$
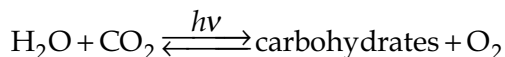
The letters $h\nu$ represent the energy of a photon; h, Planck's constant, equal to 6.6256×10^{-34} J s, is the smallest quantum of action and

has the unit of energy in Joules multiplied by time in seconds; v is the frequency of vibrations per second associated with the photon.

Many secondary and tertiary cycles and epicycles feed off, or are coupled to the primary cycle above, constituting *metabolism* in living systems. Metabolism refers to the totality of chemical reactions that make and break molecules, whereby the manifold energy transformations of living systems are accomplished. The secret of living metabolism — which has as yet no equal in the best physicochemical systems that scientists can now design — is that the energy yielding reactions are always coupled to energy requiring reactions. The coupling can be so perfect that the efficiency of energy transfer is close to 100%. Central to the coupling of energy yielding and energy requiring processes is the cyclic interconversion of adenosine triphosphate (ATP) and adenosine diphosphate (ADP). The terminal phosphate of ATP is added on to ADP by energy yielding processes such as photosynthesis and respiration. In photosynthesis, the energy of sunlight goes to excite electrons. As the electrons flow 'downhill' via a chain of electron transport proteins back to the ground state, the energy is tapped at several places along the way to make ATP from ADP. In respiration, similar processes of oxidative phosphorylation of ADP to ATP take place by using energy from the oxidation of complex foodstuffs. ATP is in turn converted into ADP in the biosynthesis of all the constituents of organisms and in all the energy transducing processes that enable them to grow and develop, to sense, to feel, to move, to think, to love, ... in short, to live (see Fig. 4.7). I leave it as an exercise for readers, if they so wish, to trace out the many metabolic cycles by a careful scrutiny of a metabolic chart of 'biochemical pathways' (an assignment normally set for intransigent students).

Coupled cycles are the ultimate wisdom of nature. They go on at all levels, from the ecological to the molecular through a wide range of characteristic timescales from millennia to split seconds. Thus, the transformation of light energy into chemical energy by green plants yields food for other organisms whose growth and

Mechanical work
(by muscle, cytoskeleton,
protoplasmic flow, etc.)

Osmotic work
(proton gradients, ion pumps)

Electrical work
(nerve conduction, membrane
potential, Na/K ATPase, etc.)

Sensory functions
(detecting light, sound, pressure
etc.)

Biosynthesis
(fats, proteins, carbohydrates)

Active transport
(ions, substrates, metabolites)

Heat generation

Signalling

ATP

ADP

hν

Oxidation of
carbohydrates,
fats, and proteins

Electron transport in
oxidative
phosphorylation

Electron transport in
photosynthetic
phosphorylation

Figure 4.7 The coupled cycles of life: energy flow in living systems. The photon energy absorbed by green plants and cycles of oxidation of foodstuffs provide mobile electrons (and protons) to make ATP; the cycles of energy charging and discharging between ATP and ADP run all the other vital activities.

subsequent decay provide nutrients in the soil on which green plants depend. The energy in foodstuffs is transformed into the mechanical, osmotic, electrical and biosynthetic work both within the plants themselves and in other organisms in all the trophic levels dependent on green plants. Each kind of energy transformation in organisms is carried out by its own particular troupe of busy molecular machines working in ceaseless cycles. And upon all of these turn the innumerable life cycles of multitudinous species that make up the geological cycles of the earth.

One is reminded of the Earth Spirit's speech in the opening scene of Goethe's *Faust*,

> In the torrents of life,
> in action's storm
> I weave and wave
> in endless motion
> cradle and grave
> a timeless ocean
> ceaselessly weaving
> the tissue of living
> constantly changing
> blending, arranging
> the humming loom of Time I ply
> and weave the web of Divinity.[19]

Energy Storage in the Biosphere

The cycling of material and energy within the biosphere automatically involves the storage, not only of material in the biosphere as biomass, but also of energy. At the beginning of this chapter, we have alluded to the large amount of energy stored in living systems, but exactly how much energy is stored? In particular, if the living system is far away from thermodynamic equilibrium, it must be free energy that is stored; for free energy disappears at equilibrium.

There have been several attempts to estimate the relative free energy content of the biosphere. One method is to compare the energy level associated with the known molecular contents of a cell with that of the appropriate mixture of small molecular weight precursors by looking up standard tables of bond enthalpies and free energies of formation that have been published for many compounds.[20] For example, Morowitz's calculations led to an estimate that the free energy level of biomass is 5.23 kcal/gm higher than the starting materials. This is approximately the energetic content of one gram of carbohydrates.[21] A slice of bread, for example, will have about

10 to 15 times this amount of energy. The *calorie* is a unit of heat energy and is equivalent to 4.184 Joules. The same kind of estimates gives values of entropy content in biomass as 0.421 cal/gm *lower* than the starting materials, so one could say that biomass has a 'negative entropy' of 0.421 cal/gm. We shall examine negative entropy in greater detail in the next chapter.

There have also been direct measurements carried out in a 'constant volume adiabatic bomb calorimeter'. This device enables us to measure the heat of combustion of substances. It consists of a tightly sealed, heavy-walled stainless steel container, thermally isolated from its surroundings. The 'biomass', usually in a dehydrated form, is placed inside the container, which is filled with O_2 at a pressure of 30 atmospheres. The combustion is started with an electrical spark through a pair of wires in contact with the biomass. A thermometer measures the heat released. From the first law of thermodynamics, the change in internal energy is equal to the heat change plus the work done:

$$\Delta U = Q + W \tag{4.13}$$

However, as the volume is constant, the work done is zero, and the decrease of internal energy is just equal to the heat released:

$$\Delta U = Q \tag{4.14}$$

These measurements give values not too dissimilar to those obtained by calculation, and represent energy enrichment on average of 0.07 eV/atom. (The electron volt eV is a unit of electric energy, especially useful in characterising electronic energy levels of atoms and molecules, it is 1.602×10^{-19} J, a very minute amount of energy.)

However, much is missing from these estimates of free energy and negative entropy content. They do not take into account the space-time organisation of the molecules into tissues, cells and organelles. This organisation corresponds in some respect, to what Morowitz[22] has referred to as the 'configurational improbability' of the living state, in addition to its 'energetic improbability'. More significantly, a lot of energy is actually stored in the organisation

of the living system. For instance, gradients and potentials involving chemical species, ions and especially protons, can readily be converted into work as fluxes and flows across membrane-bound compartments to drive the transport of metabolites or movements of cilia and flagella.

But let us take the bald estimate of the energy in biomass as a reasonable figure of the energy stored for the moment, and see what it tells us about energy flow on earth.

If we designate the average energy enrichment of biomass as ε, and the average residence time of the energy in the system as t, then the necessary flow rate per atom is,

$$f = \varepsilon/t \tag{4.15}$$

This has the same form as the chemical equation for the flow of species of atoms and molecules through a system,

$$\text{Flow of species} = \frac{\text{Total amount of the species in the system}}{\text{Mean residence time}} \tag{4.16}$$

Unlike chemical species, however, energy cannot be 'tagged', for example, with a radioactive label, and its fate followed through the system; so the residence time for energy cannot be measured directly. However, as the flow of energy into the biosphere is always accompanied by the flow of materials, especially CO_2, into the system, the mean residence time for energy can be taken as the mean residence time for carbon in the system.

The size of the various carbon pools on the surface of the earth has been estimated, giving the total biomass (both living and dead) on land and in the sea as 2.9×10^{18} gm and 10.03×10^{18} gm, respectively.[23] The values for carbon flow, i.e., the total fixed by photosynthesis per year, on land and in the ocean, are respectively, $0.073 \pm 0.018 \times 10^{18}$ gm and $0.43 \pm 0.3 \times 10^{18}$ gm.[24] Putting these values into Eq. (4.16) above gives residence times of 40 years and 21.8 years. In terms of energy, an average flow of 0.003 eV per atom of biomass per year suffices to maintain the level of the biomass. This corresponds to a total annual flow of energy of 4.8×10^{17} kcal, a value

in good agreement with the estimated yearly fixation of energy by photosynthesis, which is $13.6 \pm 8.1 \times 10^{17}$ kcal (or 5690 EJ (ExaJoule, 10^{18} J)).

An interesting question arises here: what is the significance of the long residence time of the energy that comes to the biosphere in photons from the sun? The energy of the photon meanders through innumerable cycles and epicycles of metabolism such that it is released and stored in small packets ready for immediate utilisation or in medium term depots such as gradients and fields to longer term deposits in the form of glycogen and fat, and even longer term deposits in the form of fossil fuels. The efficiency (and perhaps stability) of metabolism is associated with this drawn-out web of coupled energy transfer, storage and utilisation within the highly differentiated space-time structure of the organism and, in the case of ecological systems, the ecological communities of organisms. Metabolic and structural complexity prolongs the energy residence or storage time, perhaps by an equal occupation of *all* storage times (or all storage space-times), affording the organism an efficient and stable living.

I have indeed suggested that the equal population of energy in all space-time modes is the thermodynamic *extremum* (end state) towards which open systems evolve under energy flow, analogous to the maximum entropy state of thermodynamic equilibrium for isolated systems.[25] As distinct from isolated systems at thermody-namic equilibrium, however, the maximum entropy state of an open system is also a minimum entropy state, because all the space-time modes are effectively coupled together in a single degree of freedom. Also in contradistinction to the maximum entropy state of isolated systems where no energy is stored, the open system has a maximum of stored energy. *And as long as the energy remains stored, it can be utilised for work* (see Chapter 3). We shall have the occasion to return yet again to the importance of energy storage for vital functions in later chapters.

A similar significance may well attach to the ecological cycles as far the stability of the earth's system is concerned. There has been a great deal written on ecological sustainability and the need to preserve

genetic diversity within the past several years. Diversity may be much more important for the homeostasis — and hence sustainability — of planet earth than is generally recognised. The residence time of the energy within the biosphere is directly related to the energy stored, and hence, to species diversity or equivalently, the size of the trophic web [see Eq. (4.16)], which is the space-time organisation of the global ecological community. I have long suspected that the 'geophysiology' of planet earth is informed by same 'wisdom of the body' that is in metabolism, and this turns out to be the case, as we shall see in a later chapter.

In the next chapter, we shall examine more closely the molecular basis of energy and entropy, where it will become clear that the quantity of energy in biomass as such cannot be the whole story to the success of living organisms. It is the quality of the energy, the structure of the living system and the way energy is stored and mobilised in coupled flows and fluxes that are most crucial for life.

Notes

1. Morowitz (1968).
2. Lovelock (1979).
3. Fox (1986).
4. I was fortunate to have corresponded extensively with Sidney Fox on this issue, and we co-edited an important volume, *Evolutionary Processes and Metaphors* (Ho and Fox, 1988).
5. The account given is a simplified version of that given in Morowitz (1968) pp. 23–25.
6. See Prigogine (1962).
7. Koschmeider (1993) distinguishes between two kinds of convection cells, Bénard cells — driven by surface tension gradient — and Rayleigh-Bénard cells — driven by density gradient. The original Bénard cells, which appear as photograph or diagram in most subsequent literature, have been mistakenly interpreted as Rayleigh-Bénard cells. I thank Eric Schneider for drawing my attention to this error.
8. See Nicolis and Prigogine (1989) p. 12.
9. Nicolis and Prigogine (1989) p. 12.
10. The following account is based on that given in Morowitz (1968) pp. 29–33.

11. See Prigogine (1962, 1967); Glansdorff and Prigogine (1967); Nicolis and Prigogine (1989).
12. Haken (1977).
13. I am indebted to Kenneth Denbigh for suggesting that coherence in the living system may have something to do with the coupling of processes. This encouraged me to study Onsager's reciprocity relation more carefully and started me thinking about the consequences of coupling in equilibrium and non-equilibrium systems.
14. Onsager (1945). See Denbigh (1951) for a very clear and accessible account on which the following description is based.
15. See Westerhof and van Dam (1987), however, for a non-equilibrium thermo-dynamics treatment intended for living systems.
16. Geoffrey Sewell has recently obtained a non-linear generalisation of the Onsager reciprocity relations for a class of irreversible processes in continuum mechanics. See Sewell (1991).
17. Chandresekhar (1961), cited in Koschmeider (1993).
18. Glansdorff and Prigogine (1967) p. 159.
19. MacDonald (1989).
20. See Ho (1995a).
21. This estimate is in line with current assumptions that biomass contains 20 GJ/t of energy.
22. See Morowitz (1978) pp. 252–253.
23. Land biomass is nearly 1.5 times the estimate obtained more recently; see Ho (2006b).
24. See Morowitz (1968) pp. 68–70.
25. See Ho (1994, 1995b).