

## CHAPTER 1

# *Outline of the Main Chemical Factors in Evolution*

## 1.1 Introduction to the Chemistry of the Ecosystem

This chapter contains a general introduction to the multidisciplinary subject that includes chemistry, geochemistry, biochemistry and biology of the evolution of and on Earth, *i.e.* both the environment and its organisms. The book does depend heavily on chemistry so we give an outline of the principles of chemistry in this chapter for a reader who is not familiar with it as a discipline. Chemists may wish to skip quickly over Sections 1.2 to 1.6. In the minds of most scientists the evolution of organisms is based solely on organic chemicals, which quantitatively form by far the largest part of all living systems. In the book we wish to explore an additional part of this evolution, which in the first instance seems to be of little relevance to that of organisms. We refer to the early presence and the evolution of the inorganic surface of Earth, *i.e.* the atmospheric gases, the minerals and their solutions, mainly in the sea which, together, have formed the later changing environment for life. Here we consider these two parts of evolution, inorganic and organic, to be interacting in a common ecosystem. We will show that a major feature of life and its evolution, in addition to developing organic chemistry, is a changing availability and adopted essential use of selected inorganic chemical elements from this environment in cells. Many of these chemicals were dissolved from their minerals into solution (Table 1.1), increasingly by weathering, and then were taken into the cells of organisms.<sup>1</sup> (A cell can be looked upon as an enclosed volume of space, in part permeable to particular chemicals.) Eventually these chemicals were returned to the environment, frequently in a transformed state. These elements perform one essential role in cellular

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Evolution's Destiny: Co-evolving Chemistry of the Environment and Life

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**Table 1.1** Some Minerals from Weathering and Indirect Biological Causes

<i>Mineral</i>	<i>Source</i>
CaCO <sub>3</sub> (Mg)	Adsorption of original CO <sub>2</sub> by initial ions from the weathering of silicates
Mg <sub>2</sub> SiO <sub>4</sub>	Weathering of magnesium oxides
Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub>	The products of oxidation of Fe <sup>2+</sup> seen in Banded Iron Formations
BaSO <sub>4</sub>	Due to the oxidation of sulfide

Note. There are many other minerals formed from these two causes in small quantities

catalysis – they are required to activate the small molecules, such as H<sub>2</sub>O, H<sub>2</sub> and O<sub>2</sub>, and those in some organic metabolic cellular chemical reactions. The need for them follows from the fact that, although all organic chemicals are thermodynamically unstable relative to stable CO<sub>2</sub>, especially in the presence of the small molecules H<sub>2</sub>O and O<sub>2</sub>, they are generally kinetically quite stable at 20 °C. (Virtually all organic chemicals are kinetically unstable at >150 °C, particularly to hydrolysis and oxidation, implying that life has a restricted temperature range, that of liquid water, say from –10° to 150 °C.) At low temperature, 20 °C, they require energy input and catalysed activation in order to bring about synthesis, as well as catalysts for degradation. Therefore both energy and catalysts were required to activate organic chemicals before there could be any coded cellular chemistry, which we call life. The major catalytic inorganic ions are frequently strongly bound and of moderate or slow exchange rate in molecules. They are absolutely required. The essential role of other inorganic elements, which are poor catalysts, lies in their much weaker binding and fast exchange. These properties and the larger available quantities of these elements in the sea make them irreplaceable both in the management of osmotic and electrical balance of cells and in fast transfer of information, *i.e.* in message transmission necessary for balance between the several restricted paths of organic chemical change in cells. Later their fast transfer from outside to inside cells enabled organisms to respond quickly to rapid changes in their environment. The advantage of the exchange of some trace catalytic elements extended to their use in maintaining metabolic homeostasis inside cells. They also acted as controls of genetic expression in transcription factors.

A special chemical interest will be in the controlled biominerals (Table 1.2), produced by, even in, many organisms and giving rise to fossils,<sup>2–5</sup> as well as those made by their decomposition as deposits on the surface of Earth after death, *e.g.* the White Cliffs of Dover in the south of England and the grains of some deserts, called diatomaceous earth.<sup>5</sup> All these features of fossil and general biochemistry provide firm evidence of the coupled evolution of life with that of the surface of the Earth. We shall be led to propose that as well as the Darwinian random search amongst species of organisms for those of greatest survival value, associated with the small advantages of certain of them under given slowly changing environmental conditions,<sup>†</sup> there was and is a systematic larger-scale evolution dependent upon the opportunities which the

**Table 1.2** The Major Biominerals

<i>Mineral</i>	<i>Variations</i>
SiO <sub>2</sub>	SiO <sub>n</sub> (OH) <sub>2m-n</sub> ( $n < 2, m < 2$ )?
Ca(Mg)CO <sub>3</sub>	Various forms, many with impurities: calcite, aragonite
Ca <sub>2</sub> (OH)PO <sub>4</sub>	Apatite with impurities
SrSO <sub>4</sub>	In Acantharia (pure)
BaSO <sub>4</sub>	In a few plants
CaF <sub>2</sub>	In shrimps

Many other biominerals are listed and described in specialist publications<sup>5</sup>

large-scale evolving chemical element environment provided. It is, we believe, this strong and faster environmental development, in a given chemical direction, that guided the way to today's organisms in a systematic, overall much slower, chemical evolution.<sup>6</sup> However, the increasing complexity ruled out the possibility that they could manage it all, especially the novel oxidation chemistry and the original reductive chemistry in one compartment. As stress increased from oxidation it became necessary to produce different types of prokaryotes, bacteria, and in succession multicompartment then also multicellular organisms and mutually dependent organisms (symbiosis). Many of their evolving changes are seen in the inorganic chemical content of different organisms.

A particular problem we wish to tackle then is the changing role of the inorganic elements both in solution and in minerals in the evolution of the ecosystem. We shall observe that it is the waste by-products of the cellular organic chemistry, particularly oxygen, which initiated relatively quickly the major changes in environmental inorganic chemistry. The timing of the changes depended on their redox potential. We shall then show that it is the back-reaction of these changes which in turn affected the evolution of organisms. The two are in an interactive feedback system. In summary we have to examine the evolution of environmental and cellular inorganic with that of cellular organic/inorganic chemistry. In doing so it is extremely helpful to follow initially the geological (inorganic) chemical record of all the minerals, especially that of sediments and their impurities. The minerals include fossils, the most clear-cut evidence of organism evolution available (see Chapter 3).<sup>4</sup> To do so we divide the surface minerals of Earth into four classes.<sup>2</sup> (i) Minerals formed without any intervention of solution or biological activity, for example on the solidification of melts, magma. (ii) Mineral sediments, formed later by weathering of rocks (see Table 1.1). (iii) Minerals which have arisen from chemical transformations

<sup>†</sup> The phrase often used in this context is 'survival of the fittest', which implies competition. All we can observe is the organisms that survived at a given time and it is difficult to know the meaning of fitness, especially as the environment at a given time is unknown. The problem is illustrated by the history of the dinosaurs. We shall observe later that as organisms evolved they became mutually dependent. This indicates that it is a total system that evolves, including the environment and organisms.

of elements in the sea and where it is release of chemicals from organisms, *e.g.* oxygen, which have caused their transformation such as oxidation of iron, giving  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  precipitates,<sup>5</sup> and oxidation of sulfide to precipitated sulfur or released soluble sulfate and to release trace elements (see Table 1.1). With those chemicals from weathering, they gave the trace elements typical of the sea at a given time. (iv) Biominerals where the mineral remains attached to the cell surface or which grow internally in the organisms and are easily seen in fossils (see Table 1.2).<sup>3</sup> Confusing the issue somewhat is the production of some of the same minerals by more than one of these routes. The history of all these geological deposits has been dated in geological periods (Table 1.3), *i.e.* when a variety of surface rocks and sediments formed (see Sections 2.5 to 2.11). We shall also use this geological table with reference to the timetable of evolution of organisms and related fossils with associated chemistry in the ecosystem. As we have already noted, making the main physical–chemical connection between these minerals and living organisms is the solubility of ions from them, especially in the sea. The limiting possible changes of the inorganic content of the sea at any time arose directly from hydrothermal interaction with basalt, from weathering, or indirectly from chemical reactions of the minerals with chemicals released by cells, and from the death of organisms. We turn to which elements are of importance in the environment and of great influence upon the nature of life and its evolution.

### 1.1.1 The Involvement of the Elements in Evolution

Not all the elements of the Periodic Table (Figure 1.1) are involved in evolution to any marked degree, certainly to 1900 AD. In addition to hydrogen, carbon and oxygen we shall be concerned with the major ions of

**Table 1.3** Geological Periods

<i>Period</i>	<i>Date x 10<sup>6</sup> (yrs) ago</i>	
Archaen Eon	4,500 – 2,500	Earth Forms Prokaryotes
Proterozoic Eon	2,500 – 1,000	First Single-cell Eukaryotes Slow Oxygen Rise
Ediacaran	1,000 – 542	First Multi-cell Eukaryotes Next Oxygen Rise
Cambrian	542 – 488	Biominerals Explosion of Species
Ordovician	488 – 443	Vertebrates First Land Plants
Silurian	443 – 415	
Devonian	415 – 358	
Carboniferous	358 – 300	Coal Formation
Permian	300 – 252	First Extinction
Triassic	252 – 200	
Jurassic	200 – 150	Earliest Birds
Cretaceous	150 – 70	Seeds of Plants
Paleogene	70 – 25	
Neogene	25 →	Homo Sapiens

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
(H)																	He
Li	Be											B	(C)	(N)	(O)	F	Ne
(Na)	(Mg)											Al	(Si)	(P)	(S)	(Cl)	Ar
(K)	(Ca)	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

Bulk biological elements
  Trace elements believed to be essential for bacteria, plants or animals
  Possibly essential trace elements for some species

**Figure 1.1** The Periodic Table indicating the elements of value in organisms.

sodium, potassium, calcium and magnesium, with the anions carbonate, silicate, sulfide (later sulfate) and phosphate in the sea, all of which are also in organisms in considerable amounts. Of these ions, carbonate and sulfide/sulfate showed the greatest changes in concentration later in time. However biological activity is also generally catalysed and controlled by small amounts of ions of several other elements from the sea such as iron, manganese, cobalt, nickel, copper, zinc, molybdenum and selenium and a few others, in particular organisms, all of which have their geological sources largely in mineral oxides (silicates) and sulfides.<sup>1</sup> The availability of some of these ions, found in many biological catalysts, without which there would be no life, changed with time, as seen in sediments. We know that life today depends on some 20 elements which differ, qualitatively and quantitatively, from those which were required initially, and that they all have aqueous solutions as their biological sources, which are for the most part connected to abiotic minerals. Note that very few other elements, if any, have ever been very available in the sea. But why were so many elements needed both in catalysis and in controls of cellular activity?

As we have already stressed there are two spatial parts of chemical activity of early cells which are of particularly different concern, the zone of the internal metabolism and biopolymers and that of the external surfaces, both of which have to be synthesised with the aid of different metal ions. As we shall show, from the beginning of life the use of internal specific powerful catalysts was required in order to activate in particular oxidation/reduction and hydrolytic reactions of rather inert chemicals, *e.g.* H<sub>2</sub>, CH<sub>4</sub> and peptide molecules inside cells, while less powerful catalysts were needed for those reactions which occur relatively easily, *e.g.* hydrolysis of phosphates, inside and outside cells. The different concentrations of ions inside and outside cells

then allowed different metal ions, mostly combined with proteins, to both catalyse and control differentially parts of both internal and external metabolism. The requirement for powerful catalysts of both acid/base and redox reactions inside cells is met by the use of some of the above transition metal ions (Fe, Cu, Zn), as they are of high electron affinity and several can change valence state readily (see Figure 1.6). Moreover several can interact with inert small molecules, such as O<sub>2</sub>, in a specific, idiosyncratic way, so that we observe specific uses for them. The outside surfaces of cells are of molecules which, later in time, say approaching 0.54 Ga, are often selectively changed differently from those inside, again with the aid of strongly but differently active metal ions. They and/or more weakly active metal ions also stabilised these surface molecules. The weaker catalysis often, of acid/base reactions, was more generally executed by non-transition metal ions of lower electron affinity, for example Mg<sup>2+</sup> and Ca<sup>2+</sup>, both inside and outside cells. Lastly, bulk osmotic and electrical balance rested with bare ions of no catalytic activity (Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup>), which are in maintained gradients across boundary membranes. To preserve selective action, therefore, cells came to use a considerable variety of metal ions (see Figure 1.1), many of which changed in availability and use with time. Much of this inorganic/organic chemistry is retained in today's cells, but its beginnings are obscure.

Very little if any of the selective catalytic activity of the metal ions was or is due to the bare ions but it arose from active sites, themselves selected, in proteins, enzymes, so that the inorganic chemistry has to be considered with the synthesis of binding proteins as well as with the reactions of organic molecules in cells. One illustrative telling example of the development of external catalysed cell surface reactions, giving rise to biominerals common to later organisms, will be seen to be particularly intriguing during later evolution, because the earliest living cells did not mineralise. The earliest cells left little dependable fossil record, basically only imprints. We shall take it that biomineralisation required particular organic molecules for nucleation, growth and final form.<sup>5</sup> They arose, relatively suddenly, at a particular time of cellular and environmental chemical change. Biomineralisation is then a signature of the evolution not just of organisms but of particular organic chemistry catalysed by special metal ions, with selected binding of other metal ions and of the oxidising strength at particular times. We shall ask what happened to the environment exactly when these special metal ions and biological mineralisation arose.

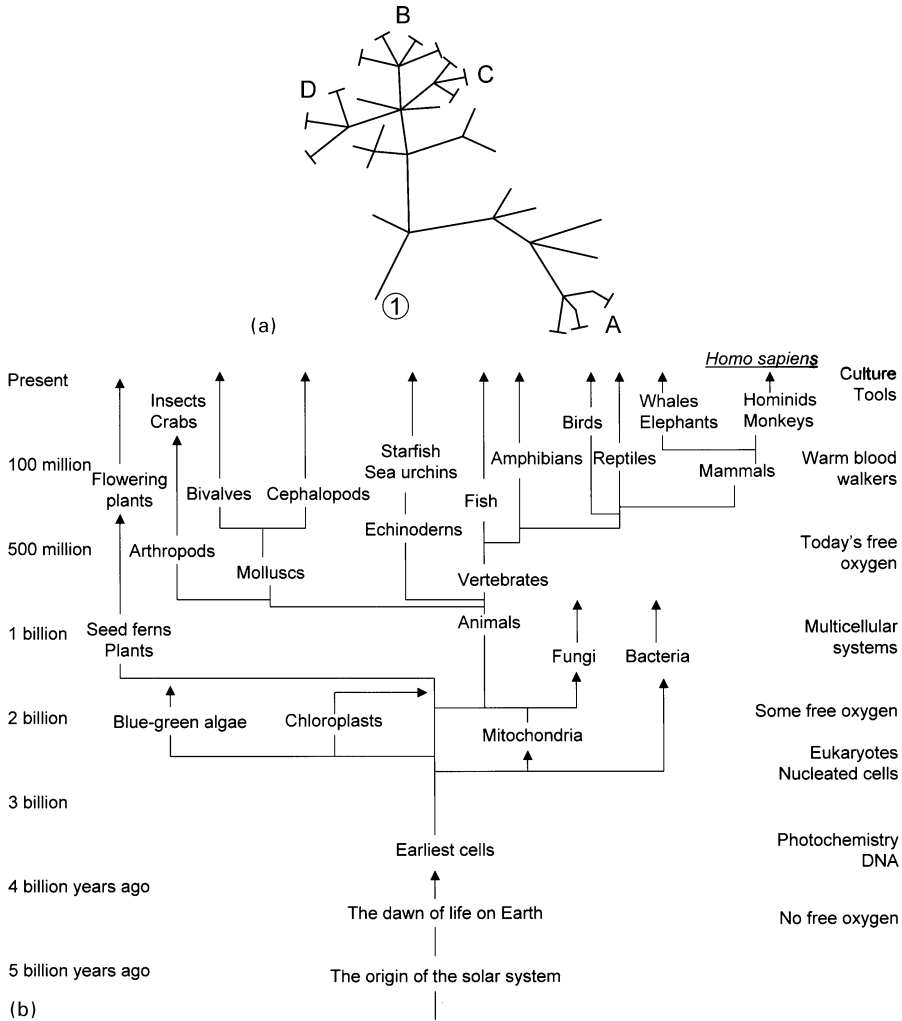
We shall also need to describe the historical development of message systems used to create and maintain control of organisation in space and in time, because at all stages of evolution both internal and external cellular activities were and are controlled by messengers. Some of these messengers are free inorganic ions (Fe<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>), but many are organic molecules often requiring catalysis for their synthesis. Now synthesis of the mainly metalloenzyme catalysts is under instruction from genes, coded information, controlled by other messengers. We can of course use knowledge of the evolution of genetic molecules (DNA and RNA), and their expression as proteins, to help examine

all selective internal changes of organic and inorganic cellular components with time. Some of the controlling free metal ion messengers interact with proteins bound to DNA, so-called transcription factors. However genetic information is poor before 0.54 Ga and it is in the period 3.5 to 0.5 Ga when the knowledge of inorganic element changes both in the environment and in cells is most reliable in providing evolutionary markers.

All cellular activity also depends on energy sources, which undoubtedly changed with time too. Both sources of materials (elements) and energy for very early living systems and their changes are probably directly or indirectly dependent upon the mineral environment and its changes from the earliest times. We shall then describe environmental evolution first from its very inorganic beginnings (Chapter 2). We shall try to keep these observed geochemical changes separate from changes in living systems as far as possible, so as to simplify understanding, but during extensive analysis of each separately we will have to bring them together to examine the whole ecosystem from very early times. To appreciate chemical evolution, therefore, we shall have to follow the analytical, chemical content of the inorganic environment with an examination of the later changing organic chemical content of organisms and its energy capture, including the genome, the proteome, the metabolome, and the metallome.<sup>1,6</sup> Later all energy was from the Sun.

Because our concern is with the environment and organism chemistry and the chemicals which go between them, we need to describe the factors that are important for maintaining the states of both the inorganic and organic chemicals. The constraints on inorganic chemistry are frequently equilibria, thermodynamic relationships which are quantitatively well-defined by constants, solubility products, complex binding constants and redox potentials (see Sections 1.3 to 1.5). The constraints on organic chemistry are quite differently, overwhelmingly, kinetics, rates of reaction, controlled by energy barriers (Section 1.6). Hence many organic chemicals have to be constantly reproduced as they decay. They are energised molecules and react very slowly. They require catalysts and extra energy to change because they are in trapped forms behind energy barriers. We describe next the limiting factors in inorganic chemistry, which give us markers of evolution from geochemistry or studies of the environment and its evolution. These limitations then allow us to make a strong connection to the manner in which organic chemistry and hence organisms could evolve.

Before we begin this analysis of the chemical evolution of an ecosystem we must pay homage to the insight and well-developed theory of life's evolution due to Darwin.<sup>7</sup> Darwin considered that organisms evolved in an ever-branching tree (Figure 1.2a).<sup>8</sup> The modern tree (Figure 1.2b) has become generally accepted as being based on survival of the fittest organisms by chance exploration and exploitation of the environment as it changed.<sup>9</sup> The tree is one of increasing diversity of biological form but must also be in each particular branch, one of increasing chemical complexity. Darwin and more recent biologists describe all this evolution in terms of species, where a species is historically connected by inherited characteristics and today by genes. Their



**Figure 1.2** (a) Darwin’s original musings on a tree of development. (b) A descriptive drawing of the modern “tree” of evolution with an outline of possible dates and of a roughly dated series of events.

discussion has been aided by the observed fossils which could be dated and we will show in Chapter 3 that this study has been greatly extended recently. Now Darwin had virtually no knowledge of the way in which organism or environmental chemistry changed. Indeed in his time there was little knowledge of chemistry. Thus by studying the chemistry of the environment and/or of organisms we can check the idea of random evolution and of an evolutionary tree while examining if it and competitive fitness are correct even in principle.\* (The idea of the tree is not an absolute requirement of natural selection.) One very important point Darwin could not have known is that the



environment changes which interact with life were systematic, as we will show, and he regarded all evolution to be without system. Survival of the fittest must be defined against the context of the environment, which we agree is changing systematically. When we examine the standing of evolution in the light of our knowledge of chemistry today, we shall class considerable differences between organisms not in terms of species but as one of chemical element differences in large groups of species, chemotypes.<sup>6</sup> Chemotypes, we will say, only arose as a consequence of systematic environmental changes, strongly implying that the dependent chemical evolution of groups of organisms has itself to be systematic, contrary to common belief. A chemotype will include many related species of organisms – genotypes. (Here we must note that a gene is related by molecular biologists to a particular stretch of DNA which is inherited and it is often assumed that therefore a species, called man for example, is completely described in its inherited characteristics by its DNA, for man the human chromosomes. In fact the chromosomes are only viable in any organism, man, with many other inherited chemical factors and even symbiotic organisms subsequent to fertilisation of a species cell. We return to the problem in Chapter 4.)

In passing it is sometimes asked if life could have arisen elsewhere. There are two separate issues. We do not have any clear idea how the great complexity of life on Earth arose. Even the very first forms of life we postulate are very complex, as we have indicated above by reference to general organism chemistry, organic and inorganic. It seems to have arisen once on Earth. Thus we do not know how to estimate the probability of it being found on another planet. Secondly we have no certain knowledge of the environmental requirements for life. What was the environment of Earth 3.5 Ga ago? We do know something of the atmosphere, rocks and sea, including the likely temperature and pressure, but we do not know if they are uniquely suitable for engendering life. Table 1.4 gives the composition of Earth in comparison with that of two other planets. There is no possibility of our kind of life on these planets. Mars is or was a better prospect, but possibly only for very primitive life. The idea that we can detect life resembling life on Earth by analyses of elements in objects, in the residues of meteorites, or on the surfaces of planets may well be misleading when we appreciate the demands of the life which have existed or do now exist on Earth. We will see that life has always required close to 20 elements in selected amounts.

In concluding this introduction we stress that our discussion of evolution is based on systematic chemistry and is quite different from other descriptions. We have indicated that the chemistry can be examined not just descriptively

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\* The phrase often used in this context is 'survival of the fittest', which implies competition. All we can observe is the organisms that survived at a given time and it is difficult to know the meaning of fitness, especially as the environment at a given time is unknown. The problem is illustrated by the history of the dinosaurs. We shall observe later that as organisms evolved they became mutually dependent. This indicates that it is a total system that evolves, including the environment and organisms.

**Table 1.4** Composition of Earth, Venus and Mercury

	<i>Earth</i>	<i>Venus</i>	<i>Mercury</i>
H ppm	33	35	0.4
C ppm	446	468	5.1
N ppm	4.1	4.3	0.05
O %	30.1	30.9	14.4
Mg %	13.9	14.5	6.5
Al %	1.4	1.4	1.1
Si %	15.1	15.4	7.0
S %	2.9	1.6	0.2
Fe %	32.0	31.1	64.4
Ni %	1.8	1.7	3.9
Ca %	1.5	1.6	1.2

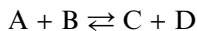
**Note** Mars is similar to Earth but has a smaller atmosphere like Venus. The outer large planets Jupiter, Saturn, Uranus and Neptune are gaseous. From J.W. Morgan and E. Anders Proc. Natl. Acad. Sci. USA, 77, 1980, 6973–6977.

but within its systematic character by a quantitative approach. By systematic we imply that the chemical changes are in large part predictable, while previous analyses of evolutionary change have been described by the phrase ‘random selection’. The distinction comes about through the connection between organism and inorganic chemistry rather than through gene changes. The reactions of inorganic compounds are often fast so that they proceed to the most stable condition, quantitative equilibrium. By contrast organic compounds react very slowly because they are unstable but trapped in long lifetime energised states. Hence we consider first the principles of changes of much of inorganic equilibrium chemistry separately from any approach to organic chemistry. Because the organic chemistry is linked to the inorganic chemistry it follows that any changes in organic chemistry will be led by the fast inorganic changes, especially those producing catalysts of organic reactions.

(Those readers familiar with the general principles of equilibria and kinetics may prefer to go immediately to Section 1.7 or to the last section of this chapter (Section 1.10), which is a summary of the main points of concern in this book.)

## 1.2 Equilibrium and Steady State Conditions

If the rates of transformation of reactants to products and those of the reverse reaction are fast enough in a given solution then the system does not store energy in C + D and is said to be at equilibrium, which we write:



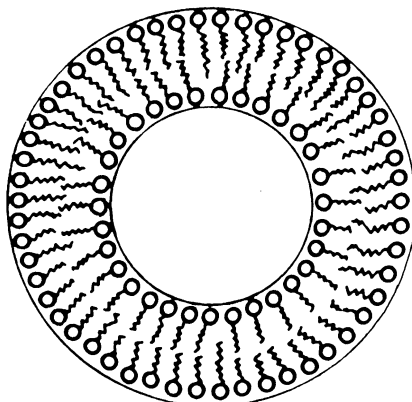
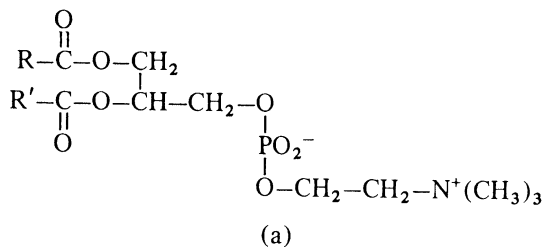
The position of balance, equilibrium, is temperature dependent. It cannot be alive or evolve: it is dead. The main equilibria that will concern us are the solubility products of compounds, complex ion stability constants, and the

standard oxidation/reduction (redox) potentials of elements and compounds in a solution.<sup>10</sup> All the cases of interest are of inorganic compounds, complexes or ions. All the solution-binding equilibria are set up relatively quickly between inorganic ions and with small organic molecules, but as we have explained, organic molecules are not in equilibria with the most stable state of their simple sources, for example  $H_2$ ,  $CO_2$ ,  $N_2$ , nor with regard to reaction with  $H_2O$  or  $O_2$ . Not all the solids of Earth are in equilibrium with their ions either. These sources are only 'stable' in a kinetic description, meaning that they have considerable but limited time of existence. In particular, apart from the large non-equilibrium temperature change from the very centre of Earth to the surface, the rapid original cooling on Earth's formation has left the surface in part in a non-equilibrium energised chemical condition. There are, however, later sediments which we may suppose came to be close to equilibrium with concentrations of components in the sea, which are governed by solubility products, complex ion and redox reaction constants. We shall have to acknowledge that there are exceptions to these generalisations. We outline the nature of the three types of equilibria: solid/solution (solubility products), complex ion formation (stability constants) and reduction/oxidation (standard redox potentials) in the next sections. The concentrations of free individual ions are then mutually dependent on the concentration of partners in these reactions and the redox conditions in the solution.

One general difficulty with both biological and geological systems is that all the material in them is in flow. The flows in biological liquids are not all fast, so that rapid exchanges can reach equilibrium (Table 1.5). Fortunately this is true for many inorganic ionic reactions and reactions of small molecules in solution with one another and with surfaces so that we can apply equilibrium considerations to them, for example incorporation of trace elements in sediments. The flow of other geological systems extends from extremely slow diffusion and movement of such bodies as tectonic plates to the faster motion of materials from volcanic activity and of the mixing of layers of the sea. Again we can select the agents we wish to discuss in these bodies so that we know which have motions fast enough to come to equilibrium locally. Other products are entirely irreversible, *e.g.* initial formation of magma from volcanoes. In many cases in both types of system the flows are strongly, constantly energised, but mixing is fast when the conditions, which are open to analysis though with some difficulty, go towards a steady state, not an equilibrium condition. A biological

**Table 1.5** Simplified Classification of Reaction Rates of Bonds

<i>Rate</i>	<i>Chemical Species</i>
Very slow	C – H, C – C, C – N, C – O, C – Halide, S = O
Slow	$PO_4R^{2-}$ , $-CO_2R$ , S – R,
Intermediate	Some complex ions <i>e.g.</i> of $Cr^{3+}$ and $Co^{3+}$ , Mn = O, Mo = O
Fast	$Mg^{2+}$ , $Ni^{2+}$
Very fast	$Na^+$ , $K^+$ , $Cl^-$ , $Ca^{2+}$ , $Zn^{2+}$ , $H^+$



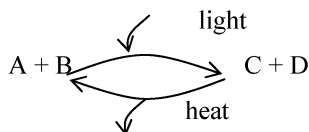
(b)

**Figure 1.3** (a) The type of molecule which forms membranes with a polar headgroup and long lipid tails of  $(\text{CH}_2)_n$ , R and R' (b) A diagram of these molecules forming a membrane around a trapped aqueous compartment, a vesicle.

cell is of this kind and can be illustrated by two aqueous phases separated by a membrane (Figure 1.3). When the membrane has pumps for ions or molecules to the inside to which energy is applied and there is an opposed flow outwards through diffusion a steady inside/outside state condition can arise. We consider the general case of a steady state next.

A very different situation from equilibrium arises if the reactants  $A + B$  are constantly energised, say by light, and then the excited condition  $C + D$  reverts slowly. Here  $C + D$  will form disproportionately relative to the equilibrium condition and we can write a final steady condition under fixed radiation by light:

In this case, which is especially relevant to our ecosystem (in particular organisms), we shall therefore need to understand physical and chemical rates



of change. The system will eventually reach a steady state in which C + D concentration can greatly exceed that at equilibrium. Such a condition stores energy. Any steady state can evolve, say through further reaction between C + D and the environment, and particularly if selective catalysts are added to the system, and which affect rates of A + B and of C + D differently. We will show that the introduction of novel catalysts, which affect rates, to organic chemical reaction systems is in fact a major part of evolution. We also show that this introduction could only occur in a systematic way in evolution. A question which arises is the length of time any such steady state of our environment with life, such as that proposed under the name Gaia,<sup>11</sup> can survive.

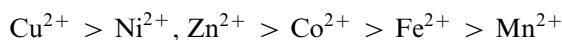
There is another way in which a partial steady state can arise, which is in part totally irreversible. Consider a flow in space of A in part to C via B. Provided there is a constant input of A at a given place it will flow steadily to B, which in part gives rise to C, which then may diffuse away and leave some of B, which returns to A, giving a steady concentration of B. B will form in a concentration around the source which does not change with time. C can be looked upon as waste. A cellular system, which is cyclic inside but rejects oxygen to the outside, is of this kind. Flowing chemicals, not said to be living, can also set up such patterns, as we shall discuss. All the flows require the irreversible use of energy and we need to consider disturbances to these flows (Section 1.9).

While organic compounds generally are energised in all their compartments (Chapter 4), inorganic ions normally equilibrate in any compartment but their free ion concentrations have energised flow between compartments (Chapters 5 and 6). It is because of the speed of their reactions in a compartment that they come to quantitative equilibria. This difference makes inorganic ions of particular value in cellular chemistry and in following evolution (see Chapters 5 and 6), because they differ from those of organic compounds in speed of response. We shall also be aware that since the Sun energises the surface of the ocean and life in it there is a continuous gradient of chemicals from the top to the solid surface at the bottom of the ocean. To make discussion simpler we shall often refer to changes of the average property of the whole ocean with time. There are also geological reservoirs of different compounds, which have become frozen or heated in different places, but we shall ignore them very largely. In any energised system of many components several different steady states may be possible but with different life times or survival strengths. Here we include the possibility of self-reproduction or multiplication, which could lead to long-term dominance of particular conditions and steady states.

With this general description of the difference between equilibrium, energised steady states only irreversible in energy, and continuous irreversible flow of energy in some materials, we now expand our descriptions, looking first at the three very important kinds of equilibrium. Those readers who have difficulty with this quantitative approach may wish to go directly to Section 1.10 where the main conclusions are given. Note that a quantitative description is a thermodynamic description and differs from previous quantitative (linear) analysis of previous approaches to evolution.

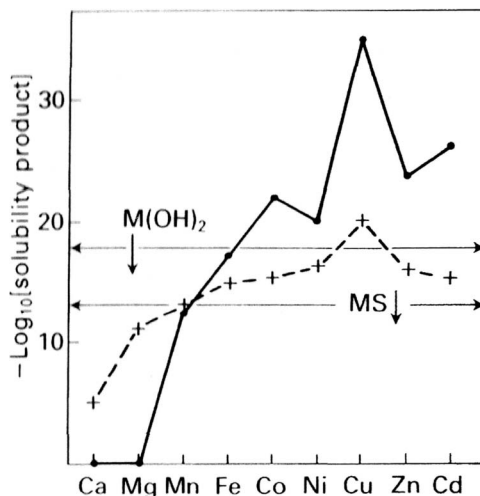
### 1.3 Solubility

General restrictions on the availability of elements as free cations,  $M^+$  and  $M^{2+}$  in the sea are insolubility and complex ion formation, especially reactions with anions. Insolubility in the very earliest sea may well have been due to silicate as well as sulfide, both of which are variable with temperature, weathering and, in the case of sulfide, oxidising conditions. Carbonates would not have been stable at high temperature of magma formation but only became so after water condensed. The hydroxides (oxides) are open to precipitation too but this is limited mainly to less common states,  $M^{3+}$  ion concentrations. The insolubility at equilibrium is described by equilibrium solubility products  $K_S = [M^{n+}][A^{n-}]$  where A is an anion. The insolubility products of salts of the abundant metal ions,  $M^{2+}$ , is that  $Ca^{2+} > Mg^{2+}$  for carbonates and phosphates but  $Mg^{2+} > Ca^{2+}$  for silicates while the order is  $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$  for sulfate insolubility. They do not form sulfides. These orders and the abundances of the elements have meant that free  $Mg^{2+}$  ions were more concentrated in the sea than  $Ca^{2+}$ . Very much later  $Ca^{2+}$  formed the major external biominerals. The general order of insolubility of salts in the series of divalent transition metal ions,  $M^{2+}$ , is



This order holds for sulfides and oxides (Figure 1.4). A major mineral in the Earth's mantle is olivine,  $Fe^{2+}Mg^{2+}SiO_4$ , which formed through the abundance of Mg and Fe (see Figure 2.1). It is thought that the early sea had high  $Mg^{2+}$  and  $Fe^{2+}$  concentrations, as olivine is relatively soluble. The high  $Fe^{2+}$  reduced the amount of sulfide somewhat as the iron precipitated it also as pyrite,  $FeS_2$ , though it too is not extremely insoluble. Even so the residual sulfide greatly restricted the free ion concentrations of Cu (probably  $Cu^+$  which has a very insoluble sulfide),  $Zn^{2+}$  and some heavier metal ions. Whereas the pyrite can enter into weathering reactions, when solubility product considerations are not so useful a guide (see Section 2.4), several of the other cation concentrations in the environment and in the consideration of biomineral formation can be usefully estimated from their solubility products. A particularly interesting feature of Figure 1.4 is the small difference in the nickel sulfide and hydroxide solubility products which is due to so-called ligand field lattice effects (see Section 2.10.2). This makes nickel of particular importance to the early life, especially in Archaea. The trace elements found in sediments are a very useful guide to the composition of seawater at any time (see Section 2.11).

The solubility of organic compounds in water is also of major concern. If we allow that before there was any life saturated C/H compounds could form then these compounds would be insoluble in water as oil, chain hydrocarbons, or gases such as methane. Some of these chain compounds could have polar end groups such as long-chain fatty acids and alcohols. In water they could form bilayers or films, which on agitation could generate bubbles with air inside or



**Figure 1.4** The logarithm of the solubility products of hydroxides, broken line, and sulfides, full line, of the divalent ions, M. The horizontal lines give the solubility limits of hydroxides at pH = 7 and for the sulfides at 1.0mM HS<sup>-</sup>, for millimolar metal ion concentrations at pH = 7.0 above which the sulfide precipitates. Compare Fig. 1.5 as both reveal a general order of metal ion binding strengths. The low value of nickel sulfide relative to its hydroxide (oxide) probably led to its early relative availability even in sulfidic conditions. From Ref. 1.

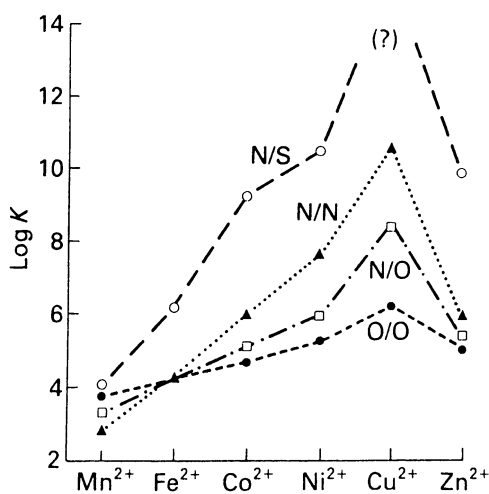
vesicles with water inside (see Figure 1.3). It is these vesicles, which we take to be the initial form of the membranes which were the progenitors of cells. The organic molecules form 'liquid' mobile barriers between aqueous phases but unlike inorganic ions they form few solids. In marked contrast the formation of inorganic solids is particularly important in Earth Sciences and also has a considerable influence on biological development of more complex organisms, but somewhat curiously in organisms it is under the influence of organic chemicals (Chapters 4 and 5). There are suggestions that inorganic minerals alone could have formed the earliest membranes, but this is impossible to test.

The insolubility of inorganic ion combinations with organic molecules is also extremely important. Many calcium combinations with particularly organic compounds produce insoluble material. Hence, as we shall see, calcium has to be kept very low in all cells.

## 1.4 Complex Ion Formation

The hydrated free ion concentrations, availability in solution, and critical for life's evolution, are related to their combinations with ligands in the sea. Here we write the equilibrium  $K = [M^{n+}][A^{n-}]/[MA]$  and note that such equilibria will hold in cells as well as in the sea as many ions react rapidly. In cells the anion A is more likely to be an organic molecule while in the sea it is an

inorganic anion. Especially in the earliest times the restriction of  $[M]$  in the sea would have been especially due to the presence of hydroxide, carbonate, silicate and sulfide but later by oxyanions of stronger acids, for example sulfate. The affinity of complex formation for first four compounds, A, are closely parallel to the above insolubility of their salts. Hydroxide and oxide greatly reduced the free ion concentrations of cations with a charge of more than two. Thus at  $\text{pH} = 7$ ,  $M^{3+}$  such as  $\text{Al}^{3+}$  could be held by  $\text{OH}^-$  in complexes or precipitates. However in the presence of silica  $\text{Al}^{3+}$  also forms large soluble aluminosilicates. Acidity, decreasing  $\text{pH}$ , increases free  $\text{Al}^{3+}$  concentration for example as in acid rain. The only divalent ion,  $M^{2+}$ , which may have been restricted by complex formation with aluminosilicate is nickel (see the solubility of nickel silicates in Section 2.11).<sup>12</sup> The later metal ions of the series  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  formed sulfide complexes of increasing strength,  $1/K$ , in this order but with  $\text{Cu}^{2+} > \text{Zn}^{2+}$ . This Irving–Williams order of binding also holds generally, but not quite universally, with organic ligands in cell compartments (Figure 1.5; compare Figure 1.4).<sup>6</sup> Now some of these elements can exist in more than one ionic cellular compartment. In particular iron is found as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and copper as  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  in complexes in different compartments of organisms, illustrating how different metal ion redox states in complexes can be present as well as different metal ions can be in separate spaces (in local different equilibrium). The ions  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  form few complexes in the sea but they have very selected partners in their complexes in cells while  $\text{Na}^+$  and  $\text{K}^+$  form hardly any complexes. Anions can also bind to one another but rarely, or to organic surfaces. We shall find stability constants of complexes of metal ions and organic ligands, including



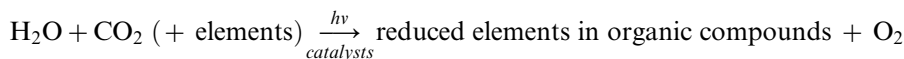
**Figure 1.5** The logarithm of the stability constants of the divalent ions in combination with organic molecules which have  $-\text{S}^-$ ,  $-\text{NH}_2$ ,  $-\text{NH}_2$  and  $-\text{CO}^-$ , and  $-\text{CO}_2^-$  only binding groups. The ordering is very important in general and in cellular chemistry. Compare Fig. 1.4. From Ref. 1.



the major biopolymers, especially proteins, of great value in estimating the free metal ion concentration but only in given compartments of cells. The reasons for the orders of selectivity of M for L in complexes are described fully in reference 1. Limitations due to rates of reaction are described in reference 12. Of particular interest in cell chemistry is that the selectivity of Figure 1.5 holds so that the thermodynamic equilibria of inorganic ions have greatly influenced chemistry, both insolubility and complex ion formation, in environmental and organism systems. As stated above the interaction with organic chemicals has had a great influence on the possibilities of evolution of the environment and life. We must mention too that some metal complex ion formation in cells is irreversible, *e.g.* with porphyrin ligands.

## 1.5 Standard Oxidation/Reduction Potentials

The major oxidation/reduction chemical changes of the surface of Earth were the uptake of carbon dioxide and nitrogen in combination with hydrogen either as H<sub>2</sub> from hydrogen sulfide or water into organic compounds, that is reduction (in cells), with release of sulfur or oxygen. The second case of O<sub>2</sub> release led to the oxidation of surface minerals and ions and molecules in solution. We shall describe the case of oxidation by ‘waste’ oxygen reaction, whence much of the environment changed. All this activity was and is driven by light aided by essential catalysts largely based on bound inorganic ions.



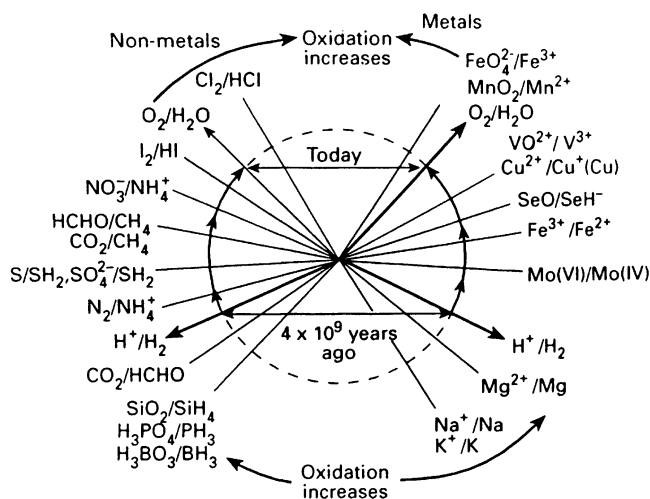
These changes, small at first, gained systematically as the rate of adsorption of light by chemicals increased. The resultant non-equilibrium systematic changes in organic chemistry will be described in Chapter 4. The changes of oxidation state, of the ‘inorganic’ elements, at first in the environment and then especially in cell catalysts and message systems, will be described in Chapters 2, 5 and 6. The metal ion oxidation changes are relatively fast and systematic due to the equilibrium thermodynamics of oxidation/reduction even if full equilibrium is not quite achieved. We write the redox potential, *E*, for the equilibrium between two redox states, say M<sup>+</sup> and M<sup>2+</sup>

$$E = E^\circ + \frac{RT}{n\mathfrak{F}} \ln \frac{[\text{M}^{2+}]}{[\text{M}^+]}$$

where *T* is the temperature,  $\mathfrak{F}$  is the Faraday and [ ] indicates concentration. *E*<sup>°</sup>, the standard redox potential for [H<sup>+</sup>]/[H<sub>2</sub>] at pH = 0 is 0.0 V and is -0.42 V at pH = 7.0. The range of possible oxidation/reduction potentials is constrained by the dominant reactions of H<sub>2</sub> at first and O<sub>2</sub> later in water, where the O<sub>2</sub>/H<sub>2</sub>O standard potential at pH = 7.0 is +0.8 V. We limit ourselves immediately to the elements rather than further consideration of them incorporated into complex chemicals as the first major development from

4.5 Ga to today of the redox states is in the sea throughout the slow switch from  $H_2$  to  $O_2$  limiting conditions and is then readily described (Figure 1.6).<sup>6</sup> This is the inevitable direction of change of element evolution and occurs in a given order in the environment, which is then a control of cell chemistry too in evolution. Some elements were directly affected by change of oxidation conditions of the sea as described while other elements were not affected by the presence of hydrogen or oxygen, for example  $Na^+$ ,  $K^+$ ,  $F^-$ ,  $Cl^-$  and  $HPO_4^{2-}$ . Further details of redox potentials are to be found in standard inorganic textbooks.<sup>12</sup> Weathering assists oxidation of the environment by exposing reduced compounds. We can observe and date oxidation most easily in the sedimentary precipitates, for example iron oxides and silicate and in sulfate deposits which incorporate radioactive elements or using the isotope fractionations of S (Section 2.7).

Radiation of the surface by the Sun increased the oxidising power of the atmosphere as water disproportionated,  $H_2$  was lost or bound to carbon and  $O_2$  was made available. Its energisation, a major subsequent part of biological chemistry, also slowly changed the oxidation condition of the equilibrated minerals of the surface and the ions in the sea as described. At the same time eruption of reduced material from deep in the Earth did from time to time reverse this process to euxinic conditions but the general oxidation direction has been preserved throughout time. Together they can introduce new elements in solution in the sea. These elements are the major driving force of evolution, they give rise to the essential novel catalysts and then reactions of



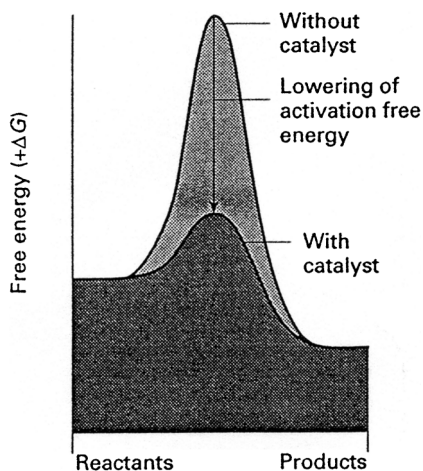
**Figure 1.6** Standard redox potentials at pH = 7.0. Also indicated is the changing value of the average redox potential of the sea before life began and today. It is this slow change which drives evolution in an orderly predictable way. From Ref. 1.

cell organic chemistry. The redox behaviour of elements is also affected by insolubility and complex ion formation of different oxidation states. As noted above, perhaps the most important interaction in the environment is that of oxygen with sulfides, giving free metal ions and eventually sulfates. One approach to the control of solubility of the metal ions in the sea with time stressed this changing control exerted by sulfide as it was removed under the influence of oxidation.<sup>1,6</sup> An improved analysis was given by Saito *et al.*,<sup>13</sup> which included sulfide complex formation (see below). The overall picture of concentrations of free ions is not greatly altered but stresses two major oxidation periods (see Chapter 6). We shall have to be careful because, as stated earlier, the sea has never been entirely uniform, that is at equilibrium at all depths with the atmosphere, although it is but one phase and has no physical barriers vertically. (We shall in our account prefer to describe the redox changes as if they were without sharp large steps.) Many cations that do not undergo redox changes themselves are affected by the presence and state of anions of non-metals which are affected by oxidation. In particular we note that amongst the elements most affected little copper can be oxidised, until after iron and sulfide have been transformed, and much zinc will also not be released until these two are removed. One other element important for life that is very sensitive to sulfide oxidation is molybdenum. From the beginning of Earth carbon dioxide was increasingly reduced by release of Ca and Mg by weathering of silicates, giving insoluble  $\text{CaMgCO}_3$ , dolomite. This weathering continued to limit  $\text{CO}_2$ , even though oxidation of methane to  $\text{CO}_2$  would have increased it.

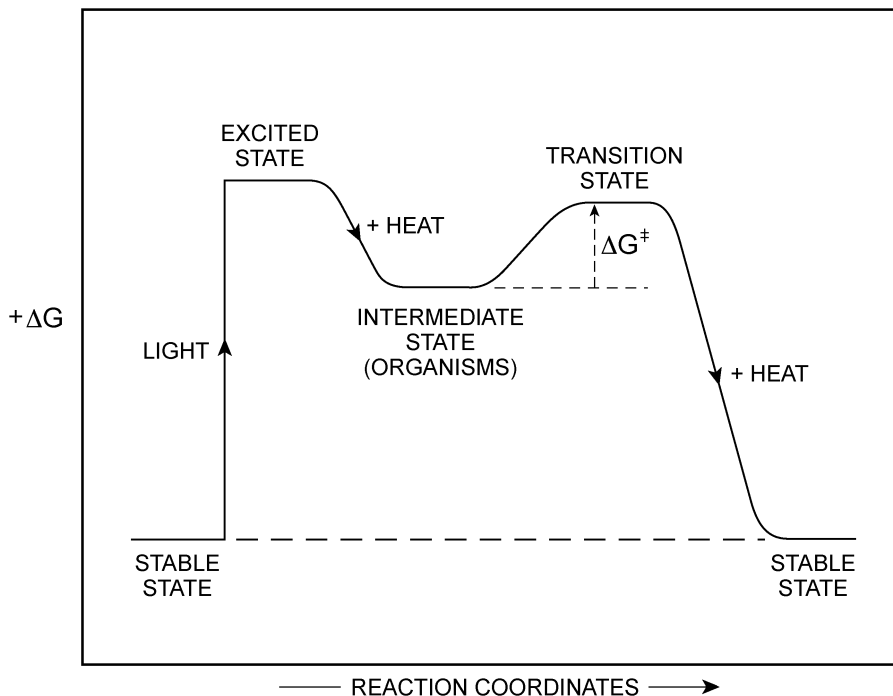
In the following parts of the book we shall find standard redox potentials of considerable value in understanding these changing oxidation conditions of the environment of vesicles and extracellular fluids as opposed to the nearly fixed controlled value of the redox potential in the cytoplasm of cells. Cells have to maintain reduced conditions for synthesis, as we shall see in Chapter 4. The implication is that it is the oxidised states of organic chemicals belonging to cells but outside the cytoplasm where we can expect the greatest evolution. The organic chemicals are never in equilibrated states so that all these three equilibria, solubility, complex formation and redox potentials, make it easy to understand inorganic reactants and products but not organic compounds at given times. Remember that generally, as equilibrium is a state of no change it alone cannot explain evolution or its rate. In the next section we consider, much more qualitatively, the nature of kinetics, that is rate of change, which is critical for evolution. The very big difference is that equilibrium constants such as solubility products, complex ion formation constants and oxidation/reduction potentials are independent of time. They are dependent on temperature but not as strongly as kinetics and we shall rarely have to describe such changes in the Earth's surface. We turn next to a somewhat deeper look at simple steady states, irreversible in energy, and flow systems, irreversible in energy and material. As we explained earlier, this requires a discussion of rates of change.

## 1.6 Rate Controls and Catalysis

It is necessary for the purposes of this book to make the role of rates of change and catalysis in evolution very clear. It returns us, in part, to the discussion of the controls on reactions of steady states, now with great emphasis on organic chemicals (Section 1.2). We begin with simple principles. Evolution is a time-dependent process which includes all rates of events in the overall physical–chemical system associated with the Sun and the Earth. It is inevitably moving toward some ultimate balanced position, which is extremely difficult to reach, before it dies. The rate of this change is inhibited by energy barriers (Figure 1.7), but is increased by catalysts or higher temperatures. In Figure 1.8, an unstable excited state system goes to the more stable ground state over barriers. Now it can easily happen that progress to the ground state can lead from energisation of an initial condition to one in long-lasting intermediate traps as in Figure 1.8. Here we consider a ground state forced to a higher energy condition by absorption of energy such as light, and on its way back, it is held temporarily but often for long periods, in an energised trap. The excited state energy of chlorophyll in Figure 4.3 avoids fluorescence or immediate energy transformation to heat loss by transferring it from an intermediate state to energised chemicals on either side of a membrane. This creates an energy gradient of extreme importance in Chapter 4. An energised trap<sup>3</sup> could also have arisen during rapid cooling of the initial state of very hot matter. For example even some of the distribution of the elements now present on Earth, which were formed at very high temperature in the giant stars, is an unstable state but which can hardly change at all on the very cool Earth (Figure 1.9),<sup>14</sup> as the energy barriers are generally too high. Changes of a few

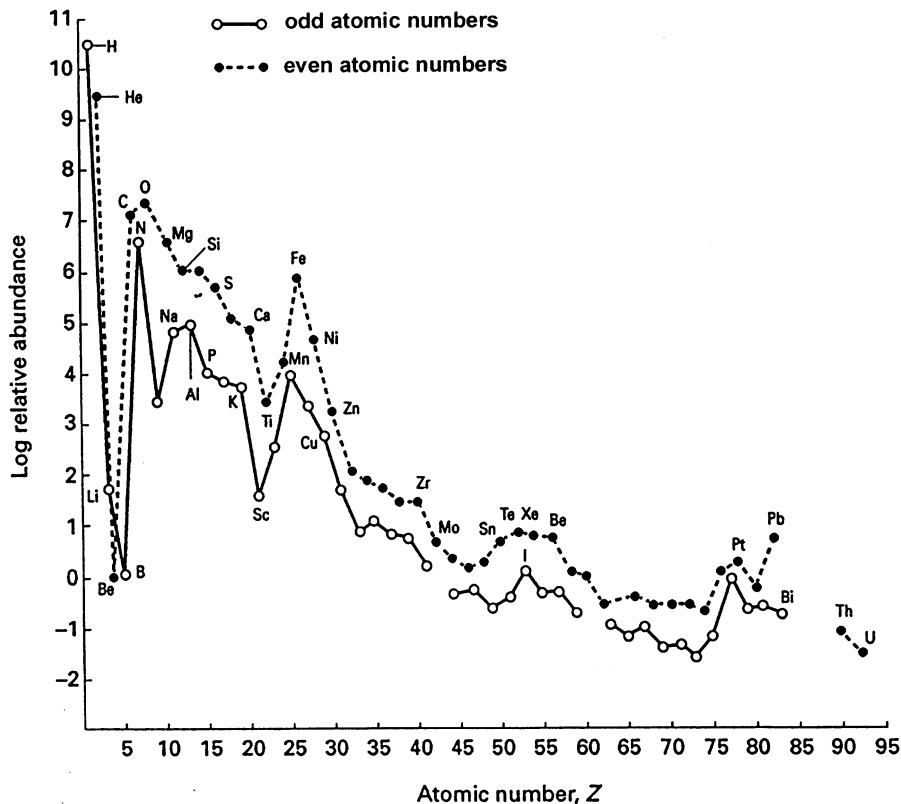


**Figure 1.7** An outline of the energy barrier,  $+\Delta G$ , to a chemical reaction and the reduction of it by a catalyst. Here the initial chemicals are of a higher energy ( $+\Delta G$ ) than the products as when a system moves toward equilibrium. The probability of crossing the barrier is related to temperature, rate  $\propto e^{(-\Delta E/RT)}$ .



**Figure 1.8** The initial (stable) state is energised for example by light and loses some energy as heat before entering an energised trap, labelled intermediate state, which can exist for a long period before crossing an activation energy barrier  $\Delta G^\ddagger$  and decaying back to the original condition giving out excess energy as heat. The intermediate state may pass through many steps of chemical change and represents an organism.

of the heaviest elements do occur, which we observe as radioactivity. These nuclear radioactive changes are not of concern here except for the fact that the extent of them allows us to date periods of time. We are deeply concerned only with the rate of change of physical and chemical element combinations in the materials around us and in organisms. Many inorganic examples involve cooling of the still hot Earth which led to, and still causes, such events as volcanoes and earthquakes and the slow decomposition of the unstable chemicals or unstable concentrations left when Earth formed. These are processes moving towards equilibrium (Figure 1.7). All such steps require energy to get over barriers and are therefore temperature, or other energisation, dependent. Extreme cold stops organic chemical change and all heat accelerates it. Of great interest in apparent contradiction to this general direction of change toward equilibrium is the production of unstable, especially organic, chemicals so obvious in organisms and the accompanying production of unstable concentrations locally of many elements within their controlled cell volumes (Figure 1.8). This case is exemplified by the intermediate state which we have labelled 'organisms'. It is largely the energy

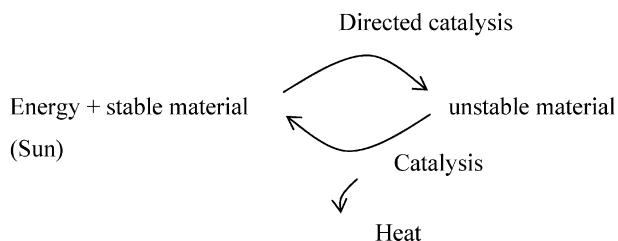


**Figure 1.9** The logarithm of the abundance of the elements on Earth. It is element availability, see Chapter 2, which is important for the connection between organisms and the environment.

of the Sun absorbed by Earth's chemicals which brings about these syntheses. Their chemical condition is metastable, inevitably unstable over time. The intermediate state is not isolated and in an environment it can change by moving over barriers before returning to the original condition. This is our basic picture of the chemistry of evolution in which the overall irreversible step is that light finally goes to heat. Weathering is another not so dramatic irreversible process produced by the Sun's energisation of water and giving rise to material in solution and then sediments (Figure 1.9). The state of organic chemicals is understandable when it is remembered that the unstable conditions of chemicals is ultimately short-lived and much is in a cycle of synthesis and degradation of material which increases the overall rate of degradation of the Sun's energy into heat.<sup>§</sup> The energy of erosion leads to

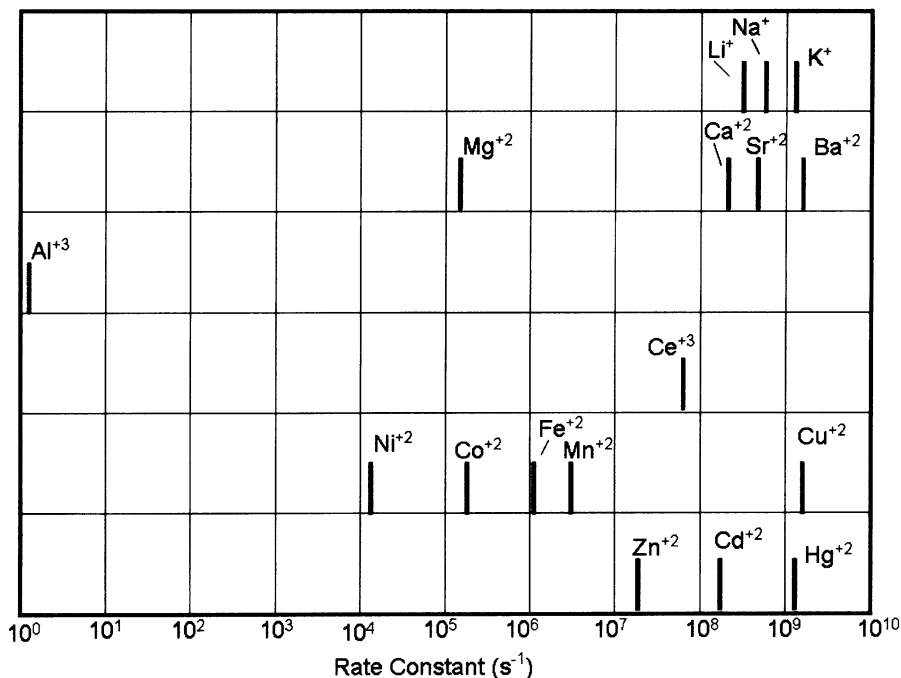
<sup>§</sup> The Sun's radiation is largely of high energy quanta, light. Heat leaving the Earth is in thermal, low energy quanta. The energy of one 'particle' (quantum) of visible light gives very many particles (quanta) of thermal energy at 20°C. The increase in the number of 'particles' gives an entropy gain which is the overall direction toward equilibrium of all spontaneous change.

precipitation and further transformation also yielding stable minerals and heat. The function of a catalyst is to increase the rate of any of these processes, both synthesis and degradation, but it does so selectively in organisms. Many of the organic processes are aided by metal ions as explained above. Catalysts can then lead quite quickly to particular molecular assemblies of great survival value. We write the scheme



These considerations could not be central to life but for the fact that the capture of energy occurs within a limited space, a cell. We shall find it necessary to divide the unstable material into chemicals organised usefully in cells (life) and waste, energised material, irreversible loss from the cell and dispersed in the environment. The dispersed chemicals, *e.g.* oxygen, react quickly going to equilibrium while the internal cell chemicals react slowly and can be built with larger units. Both of the separated chemicals are involved in further catalysed transformations. Because the new external solutions of oxidised chemicals back-interact with the cell, processing chemicals in them, the two are coupled. These remarks make it clear that an essential feature of life is directed catalysis. We shall ask which elements were used initially and at what subsequent times other elements became involved in the organisms/environment evolution. The answer shows that the presence of specific elements in the sea, a feature changing in time, is central to evolution.<sup>¶</sup> It is the change of the environment therefore that is the basic cause of evolution, preventing any long-term balanced steady state. Now the multiplicity of reactions and the need for material and energy to be distributed to all of them requires balanced exchange of material and energy within cells. Much can be done by organic molecule carriers but the inorganic ions which exchange can also ensure balance by rapid transfer and equal binding. If these ions are often bound in different catalytic molecules so that catalysis is synchronised, they have very different, faster, exchange rates themselves and are then of different control value (Figure 1.10). Most of the rates of on-reactions of inorganic ions are fast as are some of their off-rates compared to organic chemical change so

<sup>¶</sup> The importance of directed or selected catalysts is self-evident because a particular set of products is required. Selectivity is achieved through binding of reactants to defined surfaces of folded macromolecules, proteins or RNA, of defined sequences of amino acids or bases. The catalytic metal ions are held in the macromolecule frame. The control over products is clear along the chain of defined surfaces: DNA, RNA, proteins, to smaller molecules.



**Figure 1.10** Rate constants for water exchange around a variety of cations. Note how much faster the exchange is for  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$  than for  $\text{Mg}^{2+}$ . This difference is of great value in cellular communication. From Ref. 1. Exchange around  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  is fast but it is much slower around  $\text{Ni}^{2+}$ .

that in many cases equilibrium holds. For very strong binding this is not true.<sup>15</sup> Oxidation state changes are also generally fast.

Catalysis does not just apply to chemical transformation of organic molecules but as mentioned before it can be applied to the activation of precipitation. There is an energy barrier to crystal nucleation and thus precipitation of for example calcium carbonates. Particular surfaces can assist the nucleation process (or even stop it) and can be selective in the crystal form chosen, for example aragonite or calcite in shells. The presence of a biomineral is indicative of a particular synthesis of an activating organic polymer, requiring a catalyst. Shape of organisms is then defined by the controlled catalysed synthesis of polymers generally but also by controlled transfer of inorganic ions.

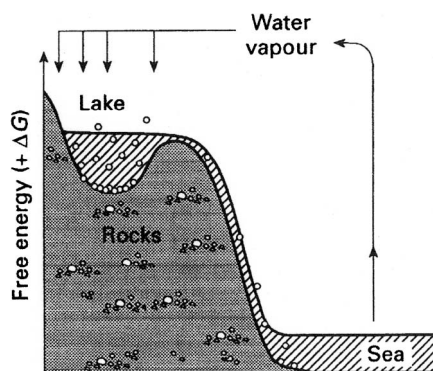
Under the various rate controls in organisms today is that bicoded information, which manages the synthesis of the whole cellular system including the catalysts. However we have to acknowledge that catalysts of a controlled kind existed before DNA or RNA coded molecules existed. It is basic to the origin of life that the solution of elements, organic and inorganic, should be energised and catalysed into synthesis paths *before* there could be coded life. As we shall discuss in Chapter 4 we know that one particular basic organic chemical



reaction scheme of proteins, nucleotides, saccharides and lipids lies at the origin of all known life but for these schemes to have arisen there must have been previous systems of high survival strength, that is high kinetic stability. Their chance of survival would have increased if on formation, the molecular products reacted further to generate bigger molecules so as to generate molecules also of high kinetic stability and with selected catalytic capacity. In effect this could give autocatalytic systems for synthesis and could be followed by a slow degradative path, see particularly the ideas of Eigen.<sup>16</sup> The cell could then gain more and more material until it was forced to break up and divide. The best possibility is controlled by timed accurate reproduction which brings us to DNA/RNA codes. We shall explore the use of codes in reproduction in Chapter 7.

Amongst the required catalysts many needed to have been inorganic ions to activate the very inert initial molecules on Earth such as  $N_2$  and  $CH_4$ . Later novel catalysts could arise either by the coded synthesis of new proteins, some to bind the existing metal ions or to bind newly introduced metal ions. At least in part this is likely to be by chance exploration of code changes, mutation, but we shall show that change itself is predated by the environment changes and we need to know if they impact on a code. The environmental inorganic changes are themselves initiated by waste from cells. Once waste is formed it has a thermodynamic unavoidable direction toward equilibrium. We must ask whether is there then an unavoidable direction to energised organic chemistry which is governed by long lifetime, due to high thermodynamic stability of molecules, but is dependent on the environment.

If we are to further our understanding of evolution we have to appreciate a further energisation of the original material present when Earth formed. This is the rate of weathering: the physical excitation of seawater to clouds and the consequential movement of material by rain (Figure 1.11). (The formation of raindrops can be catalysed by salt dust, compare biomineralisation.) The resultant weathering with oxidation by oxygen (from energisation of water)

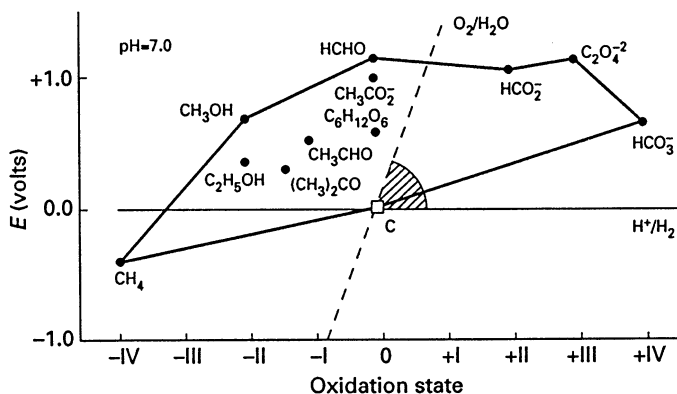


**Figure 1.11** A dynamical physical system – water flow causing weathering. Note the energy barrier. Water cycles but material transfer is irreversible giving new opportunities for life later. A lake is a physical intermediate in Fig. 1.7.

increases the amounts of catalytic chemical elements in the sea. Without much further consideration we see that this input of energy without direction is under gravity control and also leads to the irreversible degradation of minerals, giving rise to sediments which provide eventually novel regions, soils, with potential catalysts, for example, for plant growth on land. It is the subsequent role of catalysts to direct chemical and physical change both selecting synthesis and the concentrations of elements and compounds. This is the essence of the evolution of the living process in which weathering becomes central. Notice that much of weathering is not in a cycle unlike the internal chemistry of organisms in steady conditions and perhaps of the chemical content of the atmosphere.

## 1.7 The Dangers of Catalysis

We have described the importance of directed catalysis to particular products but we need to be aware of risks of more general catalysis because of the instability of organic molecules (Figure 1.12). As an example consider the reaction of oxygen with organic molecules. The eventual products are total degradation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which must be avoided, except when energy is required from, say saccharides, while cellular synthesis chemistry proceeds. Moreover, intermediate products, of initially waste oxygen reduction, such as  $\text{HO}_2^\bullet$  (superoxide) and  $\text{H}_2\text{O}_2$  (hydrogen peroxide) are more reactive than  $\text{O}_2$  and must not be free or must be destroyed quickly if life is to persist. Figure 1.12<sup>6</sup> shows that all organic C/H/O molecules are unstable to  $\text{CH}_4 + \text{CO}_2$  even in the absence of oxygen. Thus selectivity of synthesis has to be coupled with avoidance of destruction and removal of damaging agents, including other hazards such as excesses of metal ions. Cells also had to



**Figure 1.12** The redox potentials of simple organic molecules. Note that all C/H/O combinations give molecules which will disproportionate to  $\text{CH}_4$  plus  $\text{CO}_2$ , they are unstable. They are all unstable to reaction with oxygen too but they are protected from both activities by kinetic barriers.

develop protection against many novel catalytic substances in the environment. However such changes can introduce novelty in evolution.

- Introduction of a novel chemical poison, *e.g.* O<sub>2</sub> or Cu ions, in the environment either by the necessary biosynthetic reactions themselves, oxygen is an example, or by non-biological reactions such as release of Cu from geological deposits of sulfides by oxidation.
- Protection, via destruction or removal, of said chemical poison.
- Use of the chemical in novel reaction in cells, often in catalysis, which becomes essential but now in special compartments.

These steps imply that cells evolve not just to select reagents and metal ions but to manage their concentrations in particular parts of cellular space. To this end they have energised inwardly and outwardly directed pumps. We shall see this progression in the handling of newly introduced inorganic ions, especially of more or less poisonous ones, such as copper, and others which have always been present such as calcium, sodium and chloride ions but are damaging in excess in cells. The development of use of ions, original or novel, and of novel chemicals, such as oxygen in the environment to advance evolution, is then a process of energised, selective handling of transfer or of chemical change before use arose. Concentration control as well as chemical structure is an essential feature of organisms. When we couple these necessities with that of the development of coding for the novel useful activity and reproduction of life the goal of understanding the origin of life seems extremely remote. Notice that a code does not in itself allow understanding of concentration control. Here we shall assume that the initial conditions some 4 billion years ago allowed life to happen and we ask the easier question of how did its evolution come about while it was always at risk by poisons and catalysts created by its own activity?

## 1.8 Diffusion

This section applies to all parts of chemistry, inorganic and organic, during evolution. A very great difficulty with the description at various times of the conditions in the sea in which gases and ions in solutions are produced in different places is the rate of diffusion. Here diffusion rate includes loss by reaction. Some of the reactants, notably oxygen, are produced near the surface of the sea, by organisms or otherwise due to irradiation, and diffuse both upwards to form an atmosphere and downward toward the solid bottom at very different rates. Only the atmosphere is mixed rapidly. The downward 'diffusion' in the sea is more a matter of rates of reaction and of mixing of water layers to which there are considerable barriers. Environmental studies indicate that oxygen in the atmosphere could well have changed quite rapidly at around 2.5 to 2.0 Ga and again at 0.8 to 0.6 Ga. During this time, even from 2.5 to 0.8 Ga, the oxygen in the sea could have remained non-uniform with low oxygen and a low redox potential in deep water merging gradually to a high oxygen and redox potential in the surface water. The surface would then have

supported more aerobic while the deep held more anaerobic organisms for a long period. The extent of the regions probably changed slowly but, it is generally considered<sup>17</sup> that equilibration by diffusion of O<sub>2</sub> was limited until say 0.7 Ga. However even today the presence of large numbers of organisms on the surface can restrict the availability of O<sub>2</sub> and many elements there. Our problem in this book is to describe as simply as possible conditions in the sea during the whole time from about 4.5 Ga to today when we only give rough estimates at the beginning to 2.5 Ga and only reasonably good ones from 0.7 Ga to today. We shall assume for simplicity a slow change in average concentrations and of redox potential in the sea with two somewhat more rapid rises at 2.5 to 2.0 Ga and at 0.8 to 0.5 Ga. In Chapters 2 and 3 the most interesting case of limited diffusion lies in the intermediate period between these two. We shall look for markers of the changes amongst sediments.

Diffusion of gases from the atmosphere to space is more readily calculated with two important exceptions, and leads to a reasonable idea of the rate of loss of H<sub>2</sub>, CH<sub>4</sub> and He. The first exception is water which meets a definite cold final condensation trap at some 5,000 metres from the sea. Gravity then ensures its return to the sea. Its flow generates weathering assisted by oxygen and organisms. The second is oxygen which as it diffuses to the outer atmosphere, is strongly exposed to UV light, giving rise to the protective ozone layer.

The opposite 'diffusion' (mixing) from the solid bottom of inorganic ions upwards is bedevilled by the temperature gradients both vertically and horizontally despite some mixing due to eddies, tides and winds, for example. Calculations of differences between regions based on rates of formation and loss of materials as well as of diffusion have been made.<sup>17</sup>

Diffusion of low concentrations of ions or molecules in cells can be very slow, hence rates of transfer of low concentrations to give activity at a distant site requires enhanced transport. In the case of copper ions for which binding reduces the free ion to very low levels (see Figure 1.5), we shall see that carrier proteins which exchange relatively quickly aid transfer to targets which recognise the carrier. This is a very general mode for transfer for many other ions and larger organic chemicals. The carriers for small organic chemical units are frequently coenzymes, small organic molecules which carry energy too, rather than proteins.

A particularly important consideration is the combination of reaction with diffusion. The basic concept was introduced by Turing in 1952.<sup>18</sup> Reaction and diffusion can come into a steady state and we shall use the general notion in the text and several figures but we shall not attempt a mathematical analysis of such feedback systems. It is believed to play a large part in morphogenesis.

## 1.9 Irreversibility, Chaos and Predictability

Many events have a predictable nature such as the general effect of weathering due to the circulation of water (see Figure 1.11). Although the process is generally irreversible, not at equilibrium, its year-on-year activity is in weather cycles. We experience this ourselves as we live through cold, wet, hot and dry years of summer

and winter. On a larger scale the Earth has suffered climatic fluctuations over longer periods of time such as Snowball Earth events when the surface is largely covered in ice and other periods when ice virtually disappears over as long a period as several million years. Other fluctuations in weather over a shorter timescale are caused by volcanoes which can affect Earth's climate for several years. All such events have predictable consequences. Now as Belousev<sup>19</sup> and Lorenz<sup>20</sup> pointed out, although we may write equations which will indicate why these changes occur and even their long-term frequency, timing of them is quite unpredictable. The problem arises because a seemingly very insignificant event can be coupled by feedback to an ever expanding set of consequences. The usual quote is that the flapping of a butterfly's wings in one part of Earth could cause a storm thousands of miles away. These chaotic occurrences can then affect the evolution of life which has an irreversible feedback interaction with the environment. We shall draw attention to periods of large-scale unpredictable extinctions over relatively short time periods. It is expected that they could be at least partially self-correcting by feedback. In this book, however, we are little concerned with such fluctuations though they do affect the history of species, for example the disappearance of dinosaurs. We are concerned with the very long-term periods of evolution which we shall show are due to the overall degradation of energy on Earth as in the Universe, and locally that of the Sun, to low energy heat. In this process life is a rate-increasing set of chemicals as they absorb the light, becoming unstable reduced chemical bodies and then decay while they consequently produce continuous oxidation of the environment. The very nature of the overall process we shall show is a predictable general change of chemistry much though it is open to chaotic fluctuations in both very short and longer periods.

## 1.10 Summary

This book sets out to describe and analyse the nature of the chemistry on Earth's surface in inorganic atmospheric, aqueous and solid mineral phases and in organisms. Conventional wisdom keeps the two separate as inorganic and organic chemistries. We shall show that they are in fact in a strongly interactive system. In this first chapter we have introduced the major chemical elements of concern which are interactive between the two. They are given in Figure 1.1. The so-called inorganic elements, frequently metals, differ from the non-metals especially those making up the bulk of organism organic chemistry, H, C, N and O, in that we can use reversible equilibria to describe their behaviour in any particular local volume in both the environment and in organisms. The major equilibria of interest are solubility products, complex formation, and oxidation/reduction redox potentials, described in Sections 1.3–1.5. In many of their interactions between the inorganic ions themselves or with organic chemical partners, equilibria are therefore characterised by constants giving numerical value to availability. Such constants apply in organisms as well as in the environment and lead to predictable consequences. The information is of value for different conditions affecting the availability of different elements and is then

of immediate use in describing evolution of the whole system, which we shall say follows predictable conditions as availability changes.

The treatment of some inorganic element reactions and the vast majority of those of organic elements, non-metals, and compounds must be very different as they are energised. The organic chemical changes are energetically irreversible and limited by barriers to rates of change such that the major components of life are far from in equilibria. They are in energised states of considerable kinetic stability as are the waste environment chemicals from their reactive organisms. We have indicated the nature of the barriers to the activation of especially non-metal element reactions and of the barriers (see Figure 1.8), which are also important in weathering (see Figure 1.11).

There are strong feedback components between the environment and organisms in this chemistry which produces some predictable and some unpredictable behaviour, against the general trend of predictable increase in oxidative chemistry. Our view is that the unpredictable chaotic activity is not dominant in the overall predictability of evolution and we treat chaos mostly under fluctuations.

In the chapters that follow we shall outline the chemistry of evolution as follows. Earth had a long period in which life was a relatively small contribution to much of the chemistry. In fact there was no life for some 1 billion years. These 'inorganic' changes of the environment have been continuous for all the years of the planet's existence. We describe them in Chapter 2, often referring to 'weathering'. In Chapter 3 we look for the evidence of the chemistry of life of different kinds and stages of development by looking at the firmly dated discoveries of fossils. We know that much of the basis of life lies in 'organic' chemistry of H, C, N and O with some P and S which create the background to these fossils but it is extremely important to note that fossils arose at a given time after much environmental chemical change.

We have to admit that we cannot follow life's evolution directly as organisms have decayed and we have to use our knowledge of today's organisms, of fossils, and of much inferential judgement. We do not wish to use the knowledge of genetics to any great degree in Chapter 4 where we discuss this organic chemistry as simply as possible and elsewhere in the book, because we wish to describe evolution in strictly chemical terms. We consider that coded genetics could only arise after the basic organic chemicals of life had evolved. Chapter 5 returns us to the chemistry of the bulk 'inorganic' elements involved in both the environmental and cellular chemistry, especially that of Na, K, Mg, Ca and Cl. Much of it concerns the stability of cells in the sea, the way information reaches cells from the environment by fast reactions coming to equilibrium in given compartments and communication between cells in later organisms. Chapter 6 introduces the essential functions of trace elements, such as Fe and Cu, which are the major essential catalysts of the difficult reactions in cells of small molecules of H, C, N and O from the environment. There we demonstrate clearly the vital link between the changing inorganic chemistry of the environment, at close to equilibrium, with the evolution of the mixed inorganic/organic chemistry of life. These elements are also directly in the control of cellular processes. In Chapter 7

we bring all the chemistry together in an effort to demonstrate its predictability. We look for these possible links to genetics and the findings of molecular biology. Throughout we keep in mind the ‘tree of evolution’ proposed by Darwin (Figure 1.2) and we shall put it in the context of today’s knowledge of the evolution of chemistry in the total system.

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