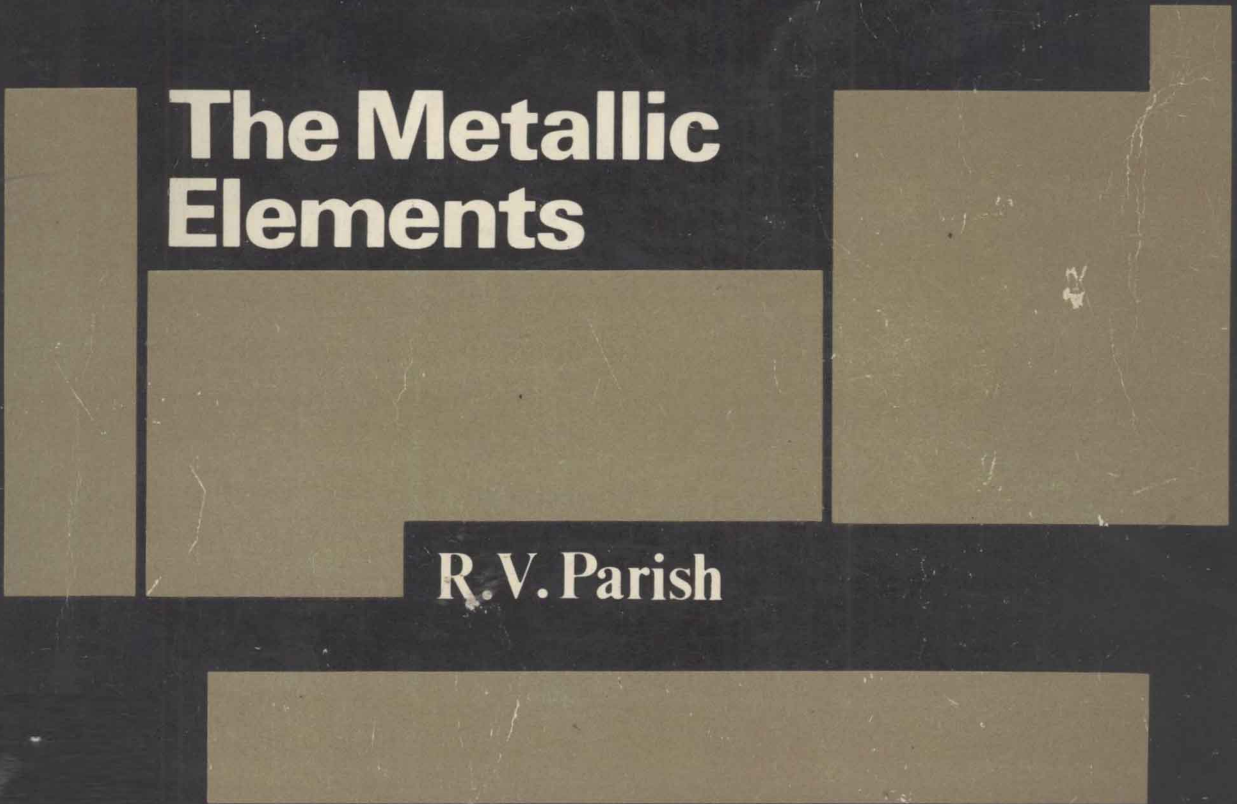

The Metallic Elements

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The metallic elements

This volume is dedicated to the late
Professor Sir Ronald S. Nyholm, F.R.S.,
(29.1.17 – 4.12.71)
whose energetic approach to inorganic chemistry
was the inspiration of many

Preface

This book is an attempt to bring together descriptive inorganic chemistry and its theoretical rationalisation. Several excellent texts already exist which cover one aspect or the other but none does both in a satisfying manner. I have also tried to avoid the pedagogic pitfall of presenting the theory first, followed by a selection of facts. Science does not work in this way, and students should be encouraged to think in a scientific fashion. In the main, therefore, the factual material precedes the rationalisations. In order to limit the factual material to manageable dimensions, I have made no attempt at a comprehensive coverage, choosing rather to examine the three most basic systems for each set of metals, viz. the halides, oxides, and aqueous chemistry. This restriction is not particularly severe, since it allows an appreciation of the ranges of oxidation states and types of bonding without burdening the text with exotic or unrepresentative material. Further study of particular elements or types of compound should follow a basic, elementary treatment of the Periodic Table as a whole. By omitting the non-metals a relatively uniform treatment of three-quarters of the known elements can be made, to which a study of the remainder could easily be added.

The rationalisation of inorganic chemistry is best achieved in thermodynamic terms, and I must acknowledge the pioneering efforts of Dasent and Johnson, whose treatments have proved invaluable. It is also a pleasure to thank my colleagues Frank Bowden and John Dwyer for their helpful criticisms of parts of the manuscript and the editor, Alan Sharpe, for his unfailing assistance.

R.V.P.

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Introductory bibliography

1. Specific references are given at the end of each chapter, but some general books require frequent citation. These are conveniently referred to by the abbreviations shown below, which will be followed by a list of chapter numbers, e.g. **HJ**, 29, 34 – chapters 29 and 34 of Heslop and Jones.

BENT – J. C. Bailar, H. J. Emeléus, R. S. Nyholm and A. F. Trotman-Dickinson (Eds.), *Comprehensive Inorganic Chemistry*, Pergamon Press, 1973. An extremely comprehensive treatment in five volumes, giving detailed coverage of the occurrence and chemistry of all the elements and also some special topics. An excellent reference text.

CW – F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edn, Wiley, 1972. A thorough, comprehensive text giving much factual information about all elements and some theoretical background in atomic structure and bonding, but very little linking of the facts to the theory. Strong on coordination chemistry and ligand-field theory.

D – W. E. Dasent, *Inorganic Energetics*, Penguin, 1970. Good, readable presentation of the application of thermodynamics to ionic, covalent and aqueous inorganic systems. Data clearly presented with some useful tabulations. Knowledge of factual chemistry assumed.

ES – H. J. Emeléus and A. G. Sharpe, *Modern Aspects of Inorganic Chemistry*, 4th edn, (previously Emeléus and Anderson), Routledge and Kegan Paul, 1973. Well-written introductory treatment of selected areas of inorganic chemistry.

H – J. E. Huheey, *Inorganic Chemistry*, Harper and Row, 1972. A well-written, thoughtful text, often raising points ignored by other authors, but an uneven and incomplete selection of topics.

HJ – R. B. Heslop and K. Jones, *Inorganic Chemistry*, Elsevier, 1976. (Formerly Heslop and Robinson, 3rd edn., 1967). Readable account of factual chemistry, with valuable introductory chapters on background theoretical aspects.

J – D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press, 1968. An excellent treatment of ionic, covalent and aqueous inorganic systems in terms of energetics. Contains much useful data. Knowledge of factual chemistry is assumed.

MM – K. M. Mackay and R. A. Mackay, *Introduction to Modern Inorganic Chemistry*, 2nd edn, International Textbook Co., 1972. Readable text giving some of the theoretical basis of inorganic systems and a fairly simple survey of factual chemistry.

PW – G. S. Phillips and R. J. P. Williams, *Inorganic Chemistry*, (2 volumes), Oxford University Press, 1965. Systematises and rationalises much inorganic chemistry but assumes a knowledge of factual chemistry. Not an easy book for the elementary student.

W – A. F. Wells, *Structural Inorganic Chemistry*, 4th edn, Oxford University Press, 1975. Comprehensive review of structures of solid inorganic compounds with useful and readable introductory chapters.

2. Other generally useful texts covering wide areas: H. F. Mark, J. J. McKetta and D. F. Othmer, *Encyclopaedia of Chemical Technology*, 2nd edn, Wiley Interscience, 1963–71. Detailed accounts of many technologically important materials and processes.
D. M. Samuel, '*Industrial Inorganic Chemistry*', *Royal Institute of Chemistry Monographs for Teachers*, No. 10, 2nd edn, The Chemical Society, 1970. Brief but useful survey of the manufacture and uses of many elements and their compounds.

3. The following older comprehensive treatments contain much useful information:
L. Gmelin, *Handbuch der anorganische Chemie*, Springer-Verlag, 1924 onwards. A series of volumes with updating supplements appearing frequently.
J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longman, 1922–37 and supplementary volumes (1958 onwards).
P. Pascal, *Nouveau Traité de Chimie Minérale*, Masson, 1956 onwards.
H. Remy, *Treatise on Inorganic Chemistry*, Elsevier, 1956.
N. V. Sidgwick, *Chemical Elements and Their Compounds*, Oxford University Press, 1950.

4. Some articles in primary or review journals will be cited. These are distinguished by using the following italicised abbreviations of the name of the journal:
Acc. Chem. Res., Accounts of Chemical Research. *Adv. Inorg. Chem. Radiochem.*, Advances in Inorganic Chemistry and Radiochemistry. *Coord. Chem. Rev.*, Coordination Chemistry Reviews. *Educ. Chem.*, Education in Chemistry. *Inorg. Chem.*, Inorganic Chemistry. *J. Chem. Educ.*, Journal of Chemical Education. *J. Chem. Soc.*, Journal of the Chemical Society. *J. Inorg. Nucl. Chem.*, Journal of Inorganic and Nuclear Chemistry. *Prog. Inorg. Chem.*, Progress in Inorganic Chemistry. *Quart. Rev.*, Quarterly Reviews (The Chemical Society). *Rev. Pure Appl. Chem.*, Reviews of Pure and Applied Chemistry.

Contents

Chapter 1

Introduction

Inorganic chemistry is the study of the structures, properties, reactivities and compounds of all the elements, excluding only the catenated compounds of carbon. Over one hundred elements are known, so that the subject is vast; it is, of course, still expanding in its own right, but it also blends imperceptibly into other disciplines such as metallurgy, biochemistry, and mineralogy, as well as being linked to other branches of chemistry through coordination chemistry and organometallic chemistry. The aim of this book is to provide a general basis of systematic inorganic chemistry onto which the other subjects can be grafted. Attempts will be made, wherever possible, to give intelligible explanations and rationalisations of the observed behaviour and, for these purposes, I believe that it is important to follow a basically scientific procedure. That is, following the 'Scientific Method', to examine the factual material first, then to look for common features and patterns in the 'data', and only then to try to explain the patterns in terms of some sort of theoretical framework. It is, of course, not possible to explain everything; the data are not always complete and there are often anomalies which are still beyond comprehension. Nevertheless, it should be possible to build up a general, logical picture and to understand some of the individual breaks in the patterns.

To provide a survey of the systematic chemistry of all the elements would be an enormous task, beyond the capacity of both reader and writer, and restrictions and simplifications are necessary to give a manageable body of material. Two limitations are therefore imposed. Firstly, only the metallic elements are considered; this eliminates only 23 elements but has the advantage that those remaining have many common characteristics, one of the most important being that much of their chemistry can be discussed in terms of simple, ionic behaviour. Secondly, no attempt is made to give a comprehensive coverage of all the types of compound formed by each metal but, by treating the same sets of systems for each group of metals (the halides, the oxides, and the aqueous chemistry), it is hoped that the similarities and differences will become apparent. The chemistry shown can then be related to the positions of the elements in the Periodic Table.

The basis of the rationalisations used will be energy. It has been said that organic and inorganic compounds differ in that the former owe their existence to kinetic effects while the latter are better understood in terms of thermodynamics. It is certainly true that all organic compounds are thermodynamically unstable in air; on the basis of energetics they would be expected to oxidise spontaneously to carbon dioxide and water, e.g.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Fortunately, this reaction does not proceed at room temperature in the absence of a catalyst, ethanol is kinetically stable (at least until after consumption!). However, in the majority of cases, simple inorganic reactions give the products expected on thermodynamic grounds, e.g. zinc dissolves in hydrochloric acid. Occasionally the anticipated reaction seems not to occur, for instance aluminium would be expected to react with air or water with the evolution of much energy, but is normally unaffected by both of these reagents. In this case, the predicted oxidation does occur but the product adheres very closely to the metal surface, protecting it from further reaction. In the main, it seems reasonable to seek thermodynamic rationales for the observed behaviour of inorganic systems. Fortunately, no more than a very elementary knowledge of thermodynamics is required; a brief introduction is given below and further guidance is available from the texts listed at the end of this chapter.

It is assumed that the reader will have a basic knowledge of the structure of the atom, the radial and angular distributions of *s*-, *p*-, and *d*-electrons, and the structure of the Periodic Table. References to these topics will also be found in the Bibliography.

Since the metallic elements have many characteristics in common, much of their chemistry can be discussed within closely related frameworks. In order to avoid much repetition, it is useful to introduce some concepts and definitions before proceeding to the detailed chemistry. The remainder of this chapter is devoted to such topics.

1.1 Metals

The first and most basic requirement is to define the **metallic elements**. Many elements are immediately recognisable as metals by characteristic physical properties, metallic lustre, conduction of heat and electricity, etc. Most of them also form simple salts, chlorides, sulphates, carbonates, etc., in which the metal is cationic. On any of these bases, the elements of the *s*-, *d*-, and *f*-blocks of the Periodic Table (Fig. 1.1) are undoubtedly metallic. The elements of the *p*-block are less easy to characterise, since this block contains elements of all types, ranging from the unequivocally metallic, like aluminium, to the equally recognisable non-metals such as oxygen, sulphur and the halogens, and even the 'noble' gases (their 'nobility' having been challenged in recent years, they will henceforth be called the 'rare' gases). Useful working criteria of metallic behaviour are the formation of cationic species in aqueous solution or the solubility of an oxide in acids (this is not the tautology it may seem, see Chapter 8). On this basis, the *p*-block metals are aluminium to thallium in Group III, germanium to lead (Group IV), antimony and bismuth (Group V). As might be expected, the borderline elements (germanium, antimony, bismuth) also have some of the characteristics of non-metals, and are often classified as semi-metals or metalloids.

Fig. 1.1 The quantum-blocks of the Periodic Table

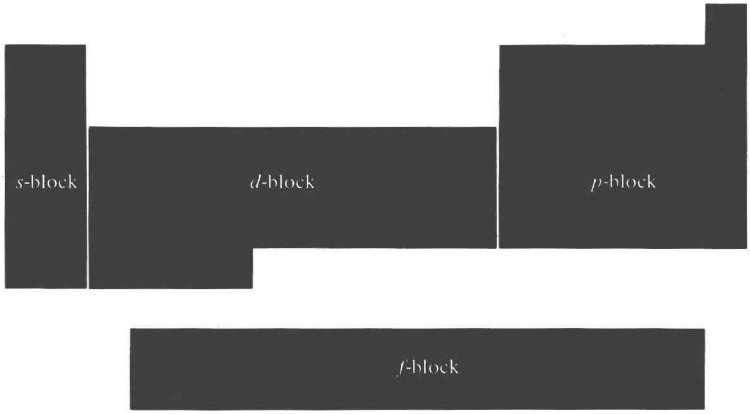


Table 1.1 Electron affinities and dissociation energies

A	**E_A/kJ mol^{-1}**	**$D(A_2)$/kJ mol^{-1}**	**A_2**
Li	−60	105	Li—Li
Be	+241	0	Be: :Be
B	−83	289	:B↑↑B:†
C	−122	630	:C=C:
N	0	946	:N≡N:
O	−142	493	$:\overset{\uparrow}{\underset{\uparrow}{\mathrm{O}}}=\overset{\uparrow}{\underset{\downarrow}{\mathrm{O}}}:$ †
F	−322	158	$:\ddot{\underset{..}{\mathrm{F}}}-\ddot{\underset{..}{\mathrm{F}}}:$
Ne	+29	0	$:\ddot{\underset{..}{\mathrm{Ne}}}:\quad:\ddot{\underset{..}{\mathrm{Ne}}}:$

† The electron configurations of the B_2 and O_2 molecules cannot be expressed simply in valence-bond terms. In each case the molecule contains two unpaired electrons which occupy a degenerate pair of molecular orbitals. In B_2 these orbitals are bonding, giving a bond order of one (two half-bonds). In O_2 the unpaired electrons are antibonding; together with the three bonding electron pairs this gives an overall bond order of two.

1.2 Ionic and covalent bonds

Two extreme types of bonding can be envisaged, ionic and covalent, and examples of each will be found in the chemistry of most metals. It is therefore useful to revise the factors which lead to the formation of each type of bond.

The electronic configuration of an atom is determined by the balance between electron–nuclear attraction and electron–electron repulsion and exchange effects. Since electrons are in continuous motion and, on average in a free atom, are distributed uniformly about the nucleus, the nuclear charge is not completely shielded in any one direction. Thus, although the net charge on the atom is zero, an external electron approaching the atom experiences an attractive potential which is often large enough for the electron to be captured and bound, forming an anion, with release of energy. The enthalpy of the process

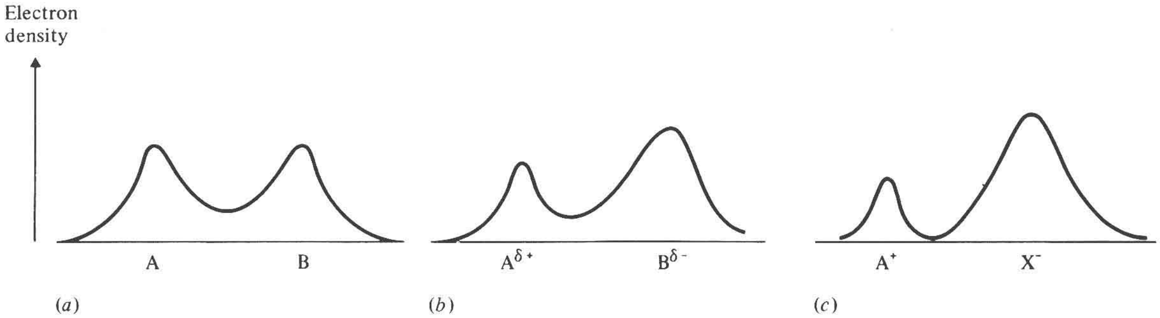
$$A(g) + e^- \rightarrow A^-(g)$$

is known as the *electron affinity* of the atom A, designated E_A; values for the elements of the second Period are given in Table 1.1. Most atoms have negative values, representing an effective positive charge at the periphery of the atom, which increases with increasing nuclear charge. Positive values are found for a few atoms which have filled or half-filled sub-shells, when the attraction is offset by unfavourable exchange and electron–electron repulsion effects.

When two atoms are brought together, the effective positive charge of each polarises the electrons of the other, particularly the relatively weakly-bound outer electrons (the valence electrons), so that electron density becomes concentrated in the region between the two nuclei. The valence electrons of each atom are now attracted by both nuclei and a stable diatomic molecule may result. This situation is often more formally described in terms of overlap of orbitals and the formation of bonding molecular orbitals giving σ- or π-bonds, but the basic binding force of the **covalent chemical bond** is the electrostatic interaction of the bonding electrons with the nuclei between which they are located. [It also appears necessary, for the formation of a stable molecule, for the valence electrons on one atom to pair spins with those of the other; if this is not possible, exchange and correlation effects keep the electrons apart and away from the internuclear region, leading to repulsion, as in Ne_2.]†

When the two atoms of a diatomic molecule are the same, the electron density is distributed equally between them and the bond is *homopolar* (Fig. 1.2a). If the two atoms are not identical, the more electronegative‡ will attract the bonding electrons more strongly. The overall electron distribution will now be asymmetric with greater electron density, and hence a fractional negative charge, on this atom. (Fig. 1.2b). The greater the electronegativity difference between the atoms, the more uneven is the charge distribution and an extreme case can be envisaged in which an electron has been transferred effectively entirely from one atom to the other, forming a wholly **electrostatic**, or **ionic bond**.

Fig. 1.2 Electron distributions in (*a*) homopolar covalent bond (*b*) heteropolar covalent bond with partial ionic character (*c*) ionic bond



On this basis it should be possible to describe any bond in terms of its ionic or covalent character. High covalent character is found in bonds between very similar atoms and becomes 100 per cent in homonuclear molecules. High ionic character is favoured by large differences in electronegativity of the atoms, and low charges and/or large radii of the ions. The last two factors affect the electric potential gradient between the ions. The higher the charges and the smaller their separation, the greater the field to which the electrons are subjected, the more the cation will polarise the anion, and the greater the covalent character of the bond. Determination of the distribution of electron densities in ionic solids clearly shows these polarisation effects (Fig. 1.3). If the bonding were 100 per cent ionic, there would be a point between the ions at which the electron density became zero, as is observed for instance in sodium chloride. In lithium fluoride, with a much smaller internuclear separation, the minimum electron density is $1{\cdot}9 \times 10^5$ e pm^{-3} ($0{\cdot}19$ e $Å^{-3}$), and the ions are clearly distorted from the expected spherical shapes.

The metallic elements have low electronegativity, are relatively easily ionised and, in their common compounds, are coupled with non-metallic elements of high electronegativity. It is frequently a good approximation to consider such compounds as being essentially ionic, with the metal forming discrete cations and the non-metal discrete anions. This *ionic model* is a very convenient basis for the discussion of the properties of these compounds, and is widely used throughout the rest of this book. It is important to realise, however, that it is only a conceptual

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† This is obviously a very incomplete description of the formation of a covalent bond; some other factors are considered in section 1.5.2. below.

‡ Electronegativity has been defined (by Pauling) as the capacity of an atom in a molecule to attract electrons to itself. It is thus not the same as electron affinity, which refers to isolated atoms. One definition (due to Mulliken) takes the average of the electron affinity and ionisation energy (see section 1.5.1) as a measure of electronegativity. In any one Period, electronegativity increases with increasing nuclear charge.

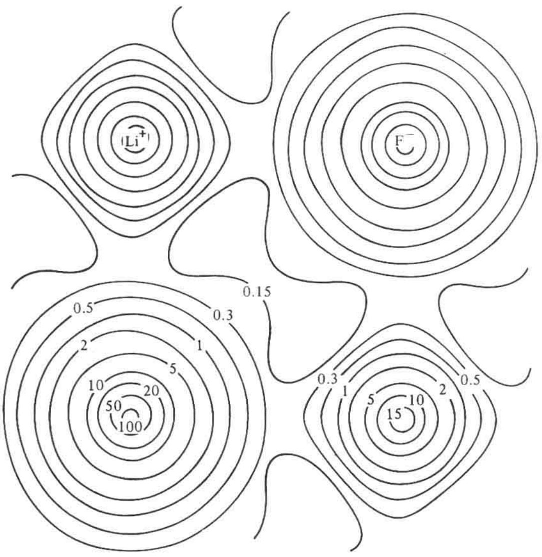

Fig. 1.3 Electron distribution in lithium fluoride. Note the distortion of the electron cloud of the cation towards the anion and the non-zero electron density between the ions (after J. Krug, H. Witte and E. Wölfel, *Z. Phys. Chem.* (Frankfurt), **4**, 36 (1955))

model which approximates to the actual state of affairs. As the charges increase and the ions become more polarising (or more polarisable) the bonding will show progressively more covalent character and departures from ionic behaviour are to be expected. The limitations of the ionic model are discussed further in section 1.4 below.

1.3 Stability and thermodynamics

'Stability' is a term which is often used rather loosely and is open to a variety of interpretations. Properly defined, of course, it is unambiguous, and suitable definition or qualification should always be given.

As mentioned earlier, there are two broad types of stability, kinetic and thermodynamic. A compound may often be unreactive under conditions in which thermodynamic considerations would indicate that reaction should occur. Chemical reactions involve the rearrangement of bonds, electrons, and atoms from a configuration of relatively low energy to another of lower energy, but the system must pass through intermediate configurations of higher energy. Thus, even though the reaction would evolve considerable energy, if there is insufficient thermal energy available for the system to surmount the energy barrier (the activation energy) no reaction will occur. Such **kinetic stability** is quite common; for instance, a mixture of carbon monoxide and air should react exothermically to form carbon dioxide, but such mixtures are indefinitely stable at room temperature unless energy is supplied in the form of a flame or a spark.

On the other hand, there may be no reaction possible, under the prevailing conditions, which would lead to a lowering in energy of the system. Such a system has **thermodynamic stability**, and it is this type of stability or reactivity which is the main concern of this book. It should be noted, however, that both types of stability have been defined in terms of a system rather than of a compound. While it sometimes happens that a compound is unstable to spontaneous decomposition, as nitrogen tri-iodide dissociates explosively to nitrogen and iodine, it is more common for a compound to react with another element or compound to form new substances. It is then not possible to define what has happened to the energy of any one component, it is the energy of the system as a whole which is lowered by reaction. It is therefore necessary to specify the composition of the mixture which may react or the type of reaction, e.g. aerial oxidation, disproportionation, reaction with acid. Thus, tin(IV) chloride, $SnCl_4$, is in some senses a stable compound, in that it will not dissociate into tin(II) chloride and chlorine or tin and chlorine, nor will it react with oxygen. It is, however, very reactive towards water, and fumes vigorously even in moist air. Thus, tin(IV) chloride is

stable with respect to dissociation
stable to atmospheric oxidation
unstable to hydrolysis.

The second of these is a kinetic effect, and this reaction will proceed at higher temperatures.

In defining the energetics of reactions, three important thermodynamic quantities must be considered, **enthalpy** (H), **free energy** (G), and **entropy** (S). For any system, it is the changes in these quantities, ΔH, ΔG, ΔS, which determine the direction and extent of the reactions which are possible. These are related by the well known expression

$$\Delta G = \Delta H - T\Delta S$$

The enthalpy is simply the heat which is liberated when the reaction is carried out at constant pressure. If the pressure is one atmosphere and the temperature 298 K (standard conditions) the standard enthalpy change is obtained, ΔH^0_{298}. A reaction which results in the liberation of heat has, by convention, a negative value for ΔH; such *exothermic* reactions result in a loss of energy by the system, and a gain by the surroundings. Reactions for which $\Delta H > 0$ are said to be *endothermic*. To a good approximation, enthalpy changes are independent of temperature.

The extent of reaction is governed by the free energy change, ΔG, which is related to the equilibrium constant by the second important relationship

$$\Delta G = -RT \ln K$$

[R is the gas constant, $8{\cdot}31\ \mathrm{J\ K^{-1}\ mol^{-1}}$, and the equilibrium constant, K, is given by the product of the concentrations (strictly the activities) of the products divided by that of the reactants, the concentrations referring to those prevailing when equilibrium has been reached

$$K = \frac{\Pi a_{\text{products}}}{\Pi a_{\text{reactants}}}$$]

At 298 K, $\Delta G/(\mathrm{kJ\ mol^{-1}}) = -5{\cdot}703 \log K$ so that, for a reaction to go essentially to completion ($K > 100$), ΔG need be only about $-12\ \mathrm{kJ\ mol^{-1}}$, a very modest value.

Unfortunately, free energies are not easy to measure, whereas enthalpy data may be obtained more readily (e.g. by direct calorimetric measurement of the heat liberated). It is often necessary, therefore, to base discussions on enthalpy data alone, and to use qualitative estimates of entropy. Entropy is more difficult to discuss simply, but it is related to the amount of freedom which a system has. The greater the number of ways in which a system can achieve the same energy, the greater the entropy. For a molecule there are contributions to the entropy from its vibrational, rotational and translational motion, so that gases generally have much higher entropies than liquids, which have greater values than solids, for which the entropies are generally very small. This leads to the commonly used assumption that a reaction in which the number of molecules increases has a positive entropy change ($\Delta S > 0$) of magnitude related to the size of the increase; entropy changes are particularly important in reactions involving the appearance or disappearance of molecules (or atoms) from the gas phase. As a (very) rough guide, ΔS is about $150\ \mathrm{J\ K^{-1}\ mol^{-1}}$ for every simple gaseous molecule formed (complex molecules can give much higher values).