Inorganic Thermodynamics

AN INTRODUCTION TO THE THERMODYNAMICS OF INORGANIC AND ORGANOMETALLIC COMPOUNDS

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N NOSTRAND REINHOLD

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An Introduction to the Thermodynamics of Inorganic and Organometallic Compounds

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Preface

Many of the textbooks relating to thermodynamics or bonding in inorganic chemistry are of a specialist type, dealing with selected areas in depth, and are unlikely to be read by undergraduate students.

We felt that there was a need for a modern up-to-date coverage of that part of thermodynamics which is relevant to bonding in inorganic compounds. As a result, we have written this selective, but introductory treatment, aimed at the undergraduate level. In addition to the more conventional topics, we have included sections on transition metal complexes, lanthanide and actinide elements, inorganic polymers, and organometallic compounds. We have used the Système International d'Unités (SI) throughout the text as is now the custom in scientific publications.

We hope that the book will be of interest to both students and teachers particularly those wishing to approach inorganic chemistry from a quantitative standpoint. References to original papers and textbooks are listed at the ends of each chapter to enable students to make a deeper study of the subject, if desired.

We thank our colleagues and wives for their assistance and tolerance during the writing of this book.

S.J.A., Exeter
G.B., Wolverhampton

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Contents

Chapter 1

Types of Bonding

1.1 Introduction

Chemistry is concerned with the interactions of atoms and molecules which comprise chemical substances. It is, therefore, of great interest to be able to make a quantitative study of these interactions. The most useful approach to such a study is through thermodynamics which is a science concerned, in part, with the measurement and calculation of the energy changes which occur during chemical reactions.

In order to make the text as self-contained as possible, we precede the discussion of thermodynamics by a brief summary of general bonding theory. A knowledge of atomic structure is assumed. Further discussions of bonding theory are to be found both in the text and in the recommended reading at the end of this chapter.

1.2 Ionic Bonding [1]

Purely ionic substances consist of cations and anions, although in the majority of cases, there is always some degree of covalent bonding. Cations can be formed most easily from those atoms which have only a weak attraction for their electrons, while anions form most readily from atoms which strongly attract electrons. Two quantities have been used to measure quantitatively these attractions – ionization energies and electron affinities respectively.

1.2.1 Ionization Energies (or Potentials)

An ionization energy may be defined as the energy required to remove completely an electron from a gaseous atom, molecule, or ion without imparting any kinetic energy to either species. Any particular species may have a series of ionization energies, referred to as the first, second, third, etc. All ionization energies of chemical interest are positive, and successive values increase since it becomes progressively more difficult to remove electrons from positive ions. We shall be concerned only with the first, second and, possibly, third ionization energies of gaseous *atoms*. A discussion of the thermodynamic aspects of ionization energies appears in Section 2.2.2.

Table 1.1. First Ionization Energies (I_1/kJ mol^{-1}) of some Representative Elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB
H 1310							He 2372
Li 519	Be 900	B 799	C 1088	N 1406	O 1314	F 1682	Ne 2079
Na 498	Mg 736	Al 577	Si 787	P 1063	S 1000	Cl 1255	Ar 1519
K 418	Ca 590	Ga 577	Ge 782	As 967	Se 941	Br 1142	Kr 1351
Rb 402	Sr 548	In 556	Sn 707	Sb 833	Te 870	I 1008	Xe 1172
Cs 377	Ba 502	Tl 590	Pb 715	Bi 774	Po –	At –	Rn 1038

The first ionization energy (I_1) of atoms does not show a regular periodic variation, as may be seen from Table 1.1. This is because at least three factors contribute to the magnitude of I_1. These are:

(a) *Atomic radius:* This is exemplified in Groups IA and IIA in which there is a steady decrease in I_1 with increasing atomic mass. The outermost *ns* electrons are subjected to an attractive potential, V, of the form

$$V = -Z_{\mathrm{eff}} \,.\, e^2/(r \,.\, 4\pi\epsilon_0)$$

In this equation, ϵ_0 is the permittivity of free space, e is the electron charge, r is the mean distance of the *ns* electron from the nucleus (assumed equal to the atomic radius) and Z_{eff} is the effective nuclear charge. The latter varies only slightly on descending Groups IA and IIA since we are dealing with electrons which lie beyond *completed* quantum shells which shield outer electrons from the nucleus quite effectively. V and, therefore, I_1 decrease in the indicated order.

(b) *Incomplete electronic shielding:* All things being equal, we might expect the increase in nuclear charge, on moving along a period to be exactly compensated by an increase in electronic shielding. This is not so, as shown in Table 1.1. In the lithium to neon period there is a *general* increase in I_1 which indicates that electrons are imperfect in shielding the outermost electrons from the nucleus.

(c) *The type of electron removed*: The increase in I_1 is, however, not smooth and we observe the sequence of ionization energies:

$$\mathrm{Li} < \mathrm{Be} > \mathrm{B} < \mathrm{C} < \mathrm{N} > \mathrm{O} < \mathrm{F} < \mathrm{Ne}$$

The discontinuities are associated with the addition of the first and fourth 2*p*-electrons respectively. The radial part of the 2*s* orbital lies partly within that of the 2*p* orbital and is said to increase the 'screening' from the nucleus of the electron in the latter. The second discontinuity is associated with the removal of an electron from an orbital which already contains one electron. In this situation electron-electron repulsions are high.

The lowest values of I_1 are found for the heavier elements of Groups IA, IIA and IIIB and it is these which most easily ionize in chemical reactions to form cations.

1.2.2 Electron Affinities

During the formation of an ionic compound from the elements, it is frequently the case that the whole or part of the energy required to form the cation is provided by the exothermic formation of the anion. The enthalpy change for the reaction in which an electron is added to a gaseous atom, molecule, or ion is known as the *electron affinity* of the species. Electron affinities, A, as defined more fully in Section 2.2.2, are usually negative quantities since most of the common ions can readily accept electrons owing to incomplete shielding of the nucleus. Positive values of A do exist, however, particularly for metals and negatively charged species. Table 1.2 lists some typical values of A for atoms and ions. Note that some texts use an electron affinity defined as the negative of our A.

From the discussion in Section 1.2.1 we expect A to be more negative for the lighter elements of Groups VB, VIB, and VIIB; this is seen to be true. It is difficult to enter into a detailed discussion of the variation in A with atomic number since electron affinities, unlike ionization energies, are not easily

Table 1.2. Electron Affinities (A/kJ mol^{-1}) of some Gaseous Atoms

F	−350	Li	−52
Cl	−365	Na	−21
Br	−342	He	+54
I	−313	Ne	+99
O	−142	O^-	+844
S	−200	S^-	+532
H	−72		
C	−121		
N	+31		

subjected to direct experimental measurement and may, therefore, be approximate in many cases.

1.2.3 Structures of Simple Ionic Substances

Crystals of ionic compounds are often highly symmetric, and this is a reflection of the highly symmetric arrangement of cations and anions which constitute such compounds.

A common feature of many ionic inorganic compounds is that the cations or anions are *close-packed.* A close-packed layer of spheres (to represent spherical ions) is shown in Fig. 1.1(a). This arrangement is the most efficient way of packing ions into a given area. A second layer can be placed on top of the first to give a layer sequence, AB. The third layer can be placed in one of two ways – coincident with layer A, or to form a layer C which is coincident with neither A nor B. In each of these stacking sequences the layers are placed such that the minimum volume is occupied. These arrangements of the close-packed layers – ABABAB etc., and ABCABCABC etc. – are called *hexagonal close-packing* (hcp) and *cubic close-packing* (ccp), respectively.

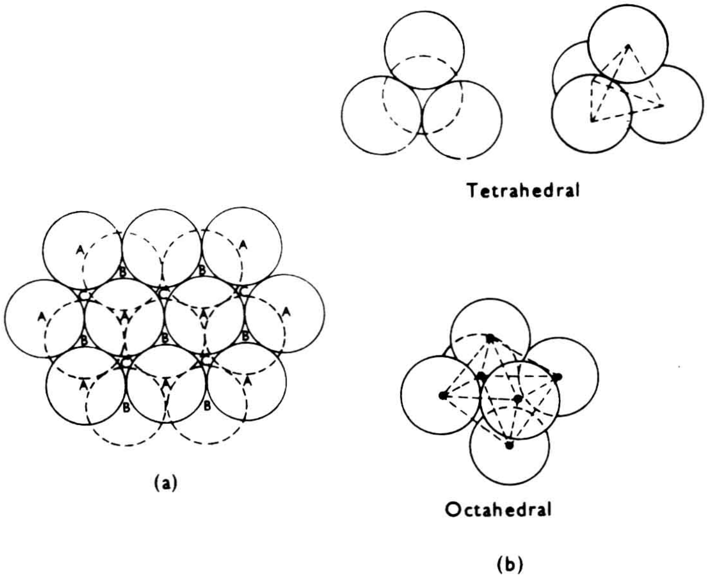

FIG. 1.1. (a) Close-Packing of spheres. Two close-packed layers are shown: AB. A third layer can be added over the A positions to give ABA or at C to give ABC sequences. (b) Types of vacant sites present in close-packed structures.

Either type of arrangement still leaves cavities between the ions. There are two types of cavity, and these are illustrated in Fig. 1.1(b). The first type is surrounded octahedrally by six spheres and is called an '*octahedral hole*'. The second type is called a '*tetrahedral hole*' and is surrounded tetrahedrally by four spheres. There are N octahedral holes and $2N$ tetrahedral holes for N close-packed spheres or ions. Some examples of ionic substances are listed below. The close-packed ion is underlined and the type of hole (oct. =

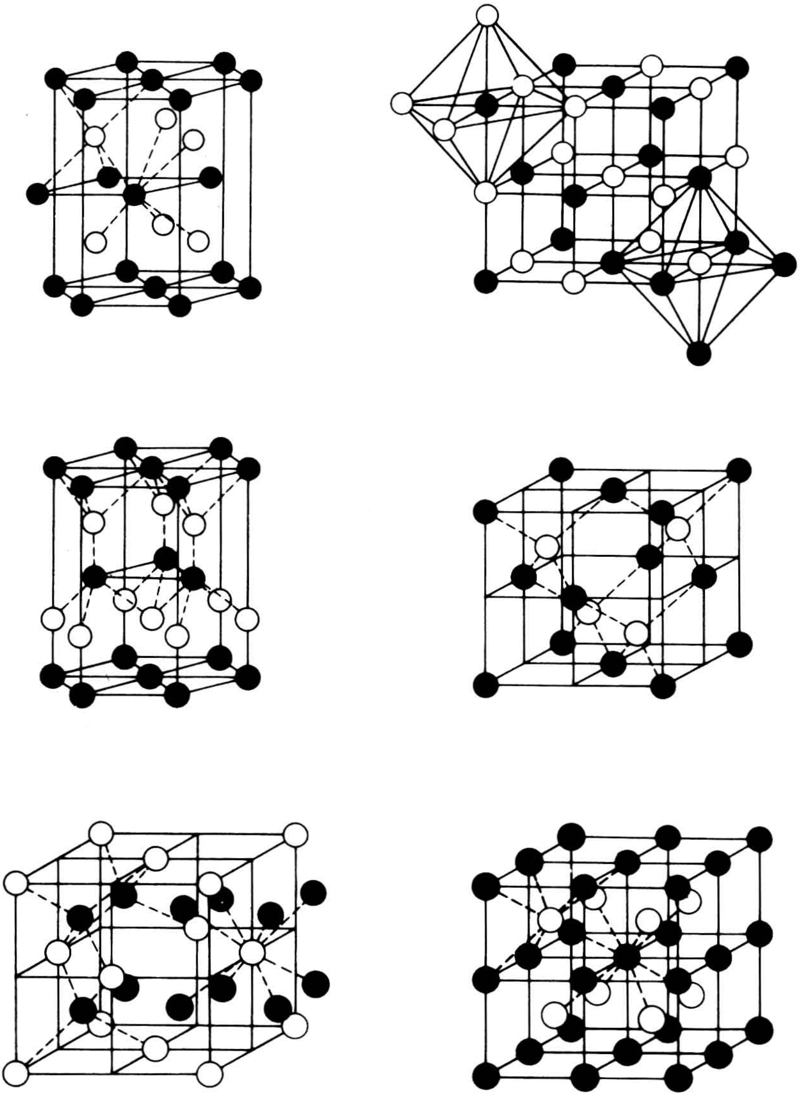

FIG. 1.2. Some representative crystal structures.

octahedral, tet. = tetrahedral), occupied by the other ion is indicated. For example, NaCl has a rock-salt structure; the Cl^- ions are cubic close-packed with the Na^+ ions in all of the octrahedral holes.

Structure	*Formula*	*Remarks*	*Examples*
Rock Salt	A^+B^- (ccp)	A^+ in oct. holes	NaCl
Zinc Blende	$A^{2+}B^{2-}$ (ccp)	A^{2+} in $\frac{1}{2}$ tet. holes	ZnS (low temp.)
Fluorite	$A^{2+}B_2^-$ (ccp)	B^- in tet. holes	CaF_2
Wurtzite	$A^{2+}B^{2-}$ (hcp)	A^{2+} in $\frac{1}{2}$ tet. holes	ZnS (high temp.)
Cadmium Iodide	$A^{2+}B_2^-$ (hcp)	A^{2+} in $\frac{1}{2}$ oct. holes	CdI_2
Cadmium Chloride	$A^{2+}B_2^-$ (ccp)	A^{2+} in $\frac{1}{2}$ oct. holes	$CdCl_2$

This is not a complete list and there are some structures which are not based on close-packed arrangements of ions. Some examples of both types are shown in Fig. 1.2 and, for a fuller discussion, the reader is referred to one of the texts listed at the end of this chapter [1].

The symmetrical arrangements of oppositely-charged ions is responsible for the high thermal stability of many ionic compounds. A more complete discussion of the energetics of ionic bonding is included in Chapter 3.

1.3 Covalent Bonding [2, 3]

When the conditions for ionic bonding, described in Section 1.2, are not satisfied, covalent bonding results if the atomic orbitals of the combining atoms can overlap sufficiently well. The wave-mechanical treatment of atoms yields a wave function, ϕ, which completely describes the behaviour of an electron in an atom. In an atom, ϕ is expressed in terms of functions which are dependent on the three spatial quantum numbers (n, l, and m) and the spin quantum number (s). The probability of finding an electron in a volume of space, dv, is given by $\phi^2\,\mathrm{d}v$. This results in the 'normalization condition',

$$\int \phi^2\,\mathrm{d}v = 1 \qquad (1.1)$$

in which the integral is over the whole of space.

A bond is formed by the overlap of adjacent atomic orbitals. A useful approximate form of the resultant *molecular orbital* is provided by a method known as the 'Linear Combination of Atomic Orbitals', abbreviated to LCAO. Within this approximation, the form of the molecular orbital, ψ, is given by equation (1.2) for a diatomic molecule, where ϕ_A and ϕ_B respresent the atomic orbitals

$$\psi = N^{-1/2}(c_A\phi_A + c_B\phi_B) \qquad (1.2)$$

centred on atoms A and B, and c_A, c_B are the numeric coefficients of each orbital. N is a normalization constant introduced to satisfy an equation similar to (1.1) and is given by

$$N = c_A^2 + c_B^2 + 2c_A c_B \int \phi_A \phi_B \mathrm{d}v \tag{1.3}$$

The last term is often neglected since usually

$$(c_A^2 + c_B^2) > 2c_A c_B \int \phi_A \phi_B \mathrm{d}v$$

If we apply (1.2) to a homonuclear molecule, then ϕ_A and ϕ_B contribute equally to ψ, and we obtain (since both positive and negative combinations are permitted)

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_A + \phi_B); \quad \psi_2 = \frac{1}{\sqrt{2}}(\phi_A - \phi_B) \tag{1.4}$$

The molecular orbital, ψ_1, is more stable than ψ_2 as can be derived from the wave equation when written in the Hamiltonian form (1.5), where E is the orbital energy

$$\mathbf{H}\psi = E\psi \tag{1.5}$$

and **H** is the Hamiltonian operator which, for a hydrogen atom, takes the following simple form:

$$\mathbf{H} = -\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{r}$$

h is Planck's constant and m_e is the mass of the electron of charge e at a distance r from the nucleus; x, y, z, are the cartesian coordinates of the electron, referred to the nucleus.

For a many-electron atom **H** is more complex, owing to inter-electron repulsive terms. Applying (1.5) to (1.2) we obtain (1.6), in which the exact form of **H** is not defined:

$$\mathbf{H}(c_A\phi_A + c_B\phi_B) = E(c_A\phi_A + c_B\phi_B) \tag{1.6}$$

Let us multiply (1.6) firstly by ϕ_A and secondly by ϕ_B and integrate over the whole of space using the conditions and notations:

$$\int \phi_A^2 \mathrm{d}v = \int \phi_B^2 \mathrm{d}v = 1 \text{ (normalization)}$$

$$S = \int \phi_A \phi_B \mathrm{d}v \text{ (overlap integral)}$$

$$\beta = \int \phi_A \mathbf{H} \phi_B \mathrm{d}v = \int \phi_B \mathbf{H} \phi_A \mathrm{d}v \text{ (resonance integral)}$$

$$\left.\begin{aligned} \alpha_A &= \int \phi_A \mathbf{H} \phi_A \mathrm{d}v \\ \alpha_B &= \int \phi_B \mathbf{H} \phi_B \mathrm{d}v \end{aligned}\right\} \text{(Coulomb integrals, equal to } \alpha \text{ for a homonuclear molecule)}$$