

2

Solid State Energetics

In Chapter 1 the differences between ionic and covalent bonding were briefly discussed. This chapter looks more closely at the principles and energetics of the **ionic model**, in particular how ions are assembled to form structures and what factors can be used to predict the stability of theoretical structures.

Aims

By the end of this chapter you should be able to:

- Describe the important properties of ionic materials
- Define the terms lattice energy, electron affinity and ionization energy
- Understand how to use the Madelung and Kapustinskii equations
- Use energy terms to determine unknown quantities and to predict likely structures

2.1 Assemblies of Ions and the Ionic Model

In Chapter 1 an ionic solid was defined as a lattice composed of anions and cations, where the atoms have lost or gained electrons to become ions. The loss or addition of electrons effectively completes a stable octet of outer electrons to create the ion.

The general structure of ionic solids results in the following properties:

1. **High melting points.** Ionic compounds contain strong non-directional interactions where the electrostatic attraction of

oppositely charged ions creates a network which requires a lot of energy to break down.

2. **Brittle.** Although ionic solids have high melting points, they also cleave relatively easily along certain directions. This can be observed from the flat faces seen in many mineralogical samples. A force sufficient to displace the ions slightly will map the negative ions on to negative ions and positive ions on to positive ions, *e.g.* in Figure 2.1 for sodium chloride, and the electrostatic forces which made the bonds previously so strong become repulsive and the material cleaves.

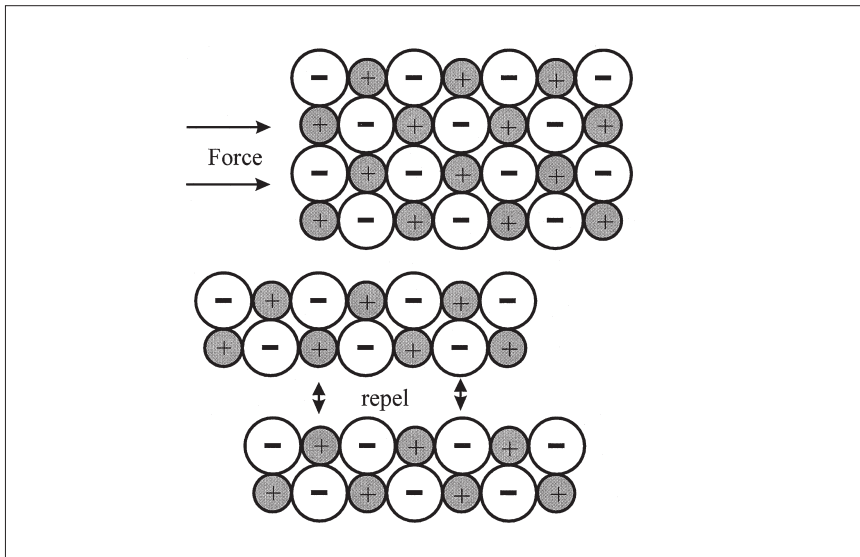


Figure 2.1 Effect of mechanical force on an ionic lattice

3. **Electrical Conductivity.** In the solid the ions are fixed on their lattice sites and electrical conductivity is poor. However, in the molten state the ions are free to move and conduct electricity in the presence of an electric field.
4. **Solubility.** Ionic compounds generally dissolve easily in polar solvents such as water. At first sight, the energy lost in breaking up the ionic lattice could be considered to be too high for dissolution; however, the solvation energy from interaction between the polar solvent and the ions, together with the increase in entropy as the lattice breaks up, compensates for the lattice energy.
5. **Coordination numbers.** Ionic compounds containing cations and anions tend to show much lower coordination numbers than metallic lattices, but higher than covalently bonded compounds. This is due to the relatively small size of the cations and relatively large size of the anions. It is not geometrically feasible to locate many large anions closely around each cation.

These properties should be treated with caution and are not definitive for ionic solids in general, since some ionic compounds do not show all these properties. For example, ammonium salts such as ammonium nitrate have low melting points (*ca.* 150–300 °C), and some compounds containing doubly charged ions such as magnesium oxide, MgO, have very low solubility.

2.1.1 Evidence for the Ionic Model

Some evidence for ionic, rather than covalent, bonding can be gathered from electron density distribution maps determined by X-ray diffraction (Chapter 3). Ions are observed as essentially spherical, highly concentrated distributions of electron density on the lattice points, with a small diffuse halo around the outside containing few electrons between the ions. This contrasts markedly with covalent bonding, where the shared electrons between the atoms generate a much higher electron density between the extremes.

Worked Problem

Q Figure 2.2 shows two schematic electron density maps for a portion of an ionic lattice and a covalent molecule. By considering each line as a contour, where closely spaced lines show changing density, which electron density map is appropriate for an ionic lattice?

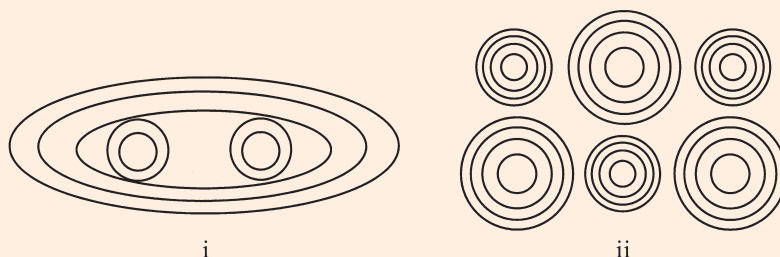


Figure 2.2 Schematic electron density maps for ionic and covalent bonding

A Diagram (ii) is the ionic lattice, as there is very low electron density between the lattice points and the contours show an essentially spherical electronic distribution.

Such experimental evidence is not always available, so determination of a compound as fundamentally ionic is usually achieved by comparison with a model: the **ionic model**. The ionic model treats an ionic solid as

an array of oppositely charged spheres held together by electrostatic (coulombic) attraction. Comparison of the thermodynamic properties of this theoretical arrangement with those determined by experiment, with a margin for experimental error, allows the compound to be classed ionic if agreement is good.

It should be noted at this stage that thermodynamic calculations are only as reliable as the experimental data placed in them. As science progresses, tabulated values for energetic terms continually change, and the most up-to-date tables should be used. Similarly, this is also true for ionic radii, which are continually being updated as the data available through use of the X-ray diffraction technique increase.

Ionization Energy

The molar **first ionization energy** is defined as the *change in internal energy at 0 K* for the process:



in which one mole of gaseous atoms becomes one mole of gaseous monpositive ions. The second ionization energy therefore involves the loss of another electron from the already positively charged ion also at 0 K, *i.e.*



Ionization energies are often referred to as **ionization potentials** and are given the unit the eV (electronvolt). This is the energy an electron requires when it falls through a potential difference of one volt (1 eV = 96.485 kJ mol⁻¹).

Several points should be noted about ionization energies. Firstly, these reactions are *always* endothermic processes, because energy is *always* required to remove an electron from an atom. Secondly, subsequent ionization energies are always greater and progressively larger than the first. It becomes more difficult to remove the negative electrons when the atom has gained one or more positive charges. Also removal of electrons reduces inter-electron repulsion: the remaining electrons become closer to the nucleus and increasingly harder to remove. Finally, this process refers to an atom in the *gas* phase. Therefore, if the material is not gaseous and atomized, additional energy must be put into the system to generate gaseous atoms before the ionization energies can be used.

As the size of the atom increases the electrons are in general easier to remove, because the outer electrons are held less tightly as they are further away from the nucleus and shielded by the inner electrons.

Table 2.1 Ionization potential for the Group 2 elements

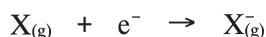
Element	Magnesium	Calcium	Strontium	Barium
1st I.P. (kJ mol ⁻¹)	738	590	550	503
2nd I.P. (kJ mol ⁻¹)	1451	1149	1064	965

Data taken from C. E. Moore, *Ionization Potential and Ionization Limits Derived from the Analyses of Optical Spectra*, National Bureau of Standards, Washington, 1970.

Therefore, the ionization energies generally decrease as a particular periodic group is descended. Table 2.1 gives the first and second ionization energies for Group 2.

Electron Affinity

The molar first **electron affinity** is defined as the energy *released at 0 K* for the process



This is somewhat confusing, as normally thermodynamics uses a negative sign to indicate an exothermic reaction and here a *positive* E_a is actually an exothermic process. An element has a positive electron affinity if the an incoming electron can enter a orbital where it experiences a strong attraction to the nucleus. For example, in the case of fluorine, only one electron is requires to complete a full outer shell and the electron affinity is +3.40 eV. Some electron affinities are summarized in Table 2.2.

In a similar way to the ionization energies, the sign of the electron affinity changes as more electrons are added. For the second and successive electron affinities, the negatively charged electrons are being added to an already negatively charged ion, and additional energy is

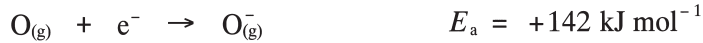
Table 2.2 Table of some elements and their electron affinities (eV)

Element	Electron affinity	Element	Electron affinity
N	-0.07	P	0.75
O	1.46	S	2.08
F	3.40	Cl	3.62
Ne	-1.2	Ar	-1.0

From H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, 1985, 14, 731.

required to overcome the electrostatic repulsion. The effect of the electrostatic interaction is overwhelming, and means that second, third and higher electron affinities are always **endothermic**, although the first electron affinity can be exothermic or endothermic.

For example, the formation of O^{2-} ions from O atoms is perhaps surprisingly endothermic, considering that under conventional terms one would expect oxygen to ‘want’ a complete octet of electrons:



Overall, formation of an oxide ion from a gaseous oxygen atom is an endothermic process of -702 kJ mol^{-1} :



It is worth pointing out that ionization energies are always *much larger* than the corresponding electron affinities, so that for any pair of species the energy required to ionize the more electropositive element is greater than the energy obtained by adding one electron to the more electronegative element (since the first ionization energy is greater than the first electron affinity). Therefore, in the gas phase, if there is no external means of gaining energy, the elements exist as *neutral atoms and not as ions*.

2.2 Lattice Formation; Electrostatic Interaction of Ions

The forces which hold an ionic idealized lattice together are entirely electrostatic, and may be calculated by summing together all the electrostatic repulsions and attractions of cations and anions in the lattice.

The attractive force (F) between a cation of charge $+z_1e$ and an anion of charge $-z_2e$ separated by a distance r , as shown in Figure 2.3, is given by Coulomb’s law:

$$F = \frac{-z_1z_2e^2}{4\pi\epsilon_0r^2}$$

where e is the charge on an electron and ϵ_0 is the permeability of free space.

The attractive potential energy (ϕ_c) of the system (the work required

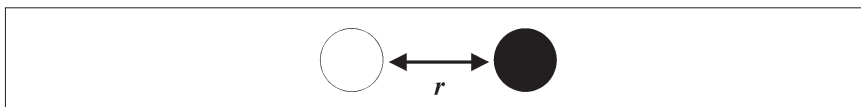


Figure 2.3 Interaction of two ions separated by the distance r

to go from $r = \infty$ to some value of r) can be determined by integrating this equation over the limits $r = \infty$ to $r = r$ with respect to r , giving

$$\phi_c = \frac{-z_1 z_2 e^2}{4\pi\epsilon_0 r^2}$$

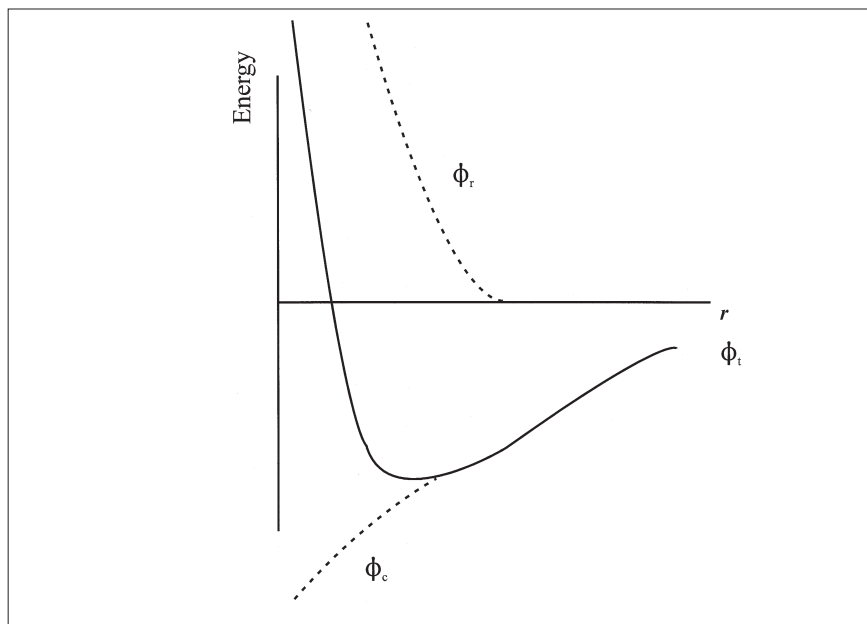


Figure 2.4 Overall attractive energy (ϕ_t) resulting from the electrostatic interaction of two ions

This expression produces the graph shown in Figure 2.4 for two ions being brought together from infinity. Clearly the ions are preventing from coalescing at $r = 0$ by some repulsive force. A repulsive force is set up owing to ‘overlap’ of the filled electron shells of the ions. The system comes to equilibrium where the attractive force is balanced by the repulsive force, which can be modelled using the expression:

$$\phi_r = be^{-r/\rho}$$

where b and ρ are constants, r is the distance between the two ions and ϕ_r is the repulsive term. Then:

$$\phi_{\text{total}} = \phi_c + \phi_r = \frac{-z_1 z_2 e^2}{4\pi\epsilon_0 r} + be^{-r/\rho}$$

Differentiation of this expression with respect to r , where the repulsive and attractive forces are in equilibrium, produces the Born–Lande potential for one pair of ions. For one mole of ions the expression must be multiplied by Avogadro’s number (N_A).

This equation now gives the energy required to generate one mole of ion pairs each separated by the equilibrium value of r (r_0) from the gaseous ions brought together from infinity. This is opposite in sign and equal in magnitude to the **lattice energy** (U_L) which is defined as the *change in internal energy at 0 K when one mole of crystals breaks down into constituent ions in the gas phase*:



Using this definition, since appropriately charged ions are being separated, the value of U_L is always positive (*i.e.* breaking of an ionic lattice is always endothermic).

The **Madelung constant**, A , is also added to the equation. This is a factor which takes into account *all* the interactions between the ions, since an ion in a lattice is influenced by more than just one other single ion of opposite charge, as considered above. Fortunately, these attractions and repulsions form a mathematical series which depends on the lattice type. The values of the Madelung constant have been calculated by computer and some are shown in Table 2.3. The final expression of the Born–Lande equation then becomes:

$$U_L = \frac{AN_A z_1 z_2 e^2}{4\pi\epsilon_0 r_0} \left[1 - \frac{\rho}{r_0} \right]$$

The equation can then be used to calculate lattice energies, providing the Madelung constant is known and the minimum distance between cation and anion can be calculated.

Table 2.3 Madelung constants for selected structures

Lattice type	Coordination numbers	Madelung constant
Sodium chloride	6:6	1.74756
Calcium fluoride	8:4	2.51939
Zinc blende	4:4	1.63806
Wurtzite	4:4	1.64132
Rutile	6:3	2.408
Caesium chloride	8:8	1.76267

Worked Problem

Q Using the Born–Lande equation, determine the lattice energy of sodium chloride given that $\rho = 34.5$ pm.

A From the table, $A = 1.74756$, the cell parameter of sodium chloride is 5.63 \AA (563 pm), so the minimum distance between sodium and chloride is just 281.5 pm (half the cell edge, see Figure 1.14). The charge on both ions is one. Therefore

$$U_L = \frac{1.748 \times 6.022 \times 10^{23} \times 1 \times 1 \times (1.602 \times 10^{-19})^2}{4 \times 3.14 \times 8.854 \times 10^{-12} \times 281.5 \times 10^{-12}} \left[1 - \frac{34.5 \times 10^{-12}}{281.5 \times 10^{-12}} \right] \text{ J mol}^{-1}$$

$$U_L = 863[1 - 0.123] = +757 \text{ kJ mol}^{-1}$$

Although in this example we can easily calculate the inter-ion distance in sodium chloride, the value of r_0 can also be estimated from tabulated ionic radii.

There is much confusion about the definition of lattice energy. In some textbooks it is described in terms of the formation of the lattice *from* the gaseous ions. Throughout this text the lattice energy will be described as a positive endothermic quantity which involves *the separation of ions (bond breaking)* rather than lattice formation.

The use of the Born–Lande equation requires the structure type to be known, as the Madelung constant for a specific structure is used in the equation. If the structure of the theoretical compound is not known, or the Madelung constant is not readily available, the lattice energy can be *estimated* using the Kapustinskii equation:

$$U_L = \frac{(1.214 \times 10^5) V z_1 z_2}{r_1 + r_2} \left[1 - \frac{34.5}{r_1 + r_2} \right]$$

where z_1 and r_1 are the charge and radius of the first ion, z_2 and r_2 are the charge and radius of the second ion and V is the number of ions in the formula of the compound. This expression uses the fact that the Madelung constant is similar for compounds with the same coordination numbers. For example, sodium chloride has 6:6 coordination, and zinc blende has 4:4 coordination; in each compound both cation and anion have the same coordination number. Both sodium chloride and zinc blende have Madelung constants about 1.7, as do wurtzite and caesium chloride.

Worked Problem

Q Use the Kapustinskii equation to calculate an approximate lattice energy for calcium chloride, CaCl_2 .

A $r^+(\text{Ca}) = 100 \text{ pm}$, $r^{\ominus}(\text{Cl}) = 181 \text{ pm}$, $V = 3$ and $r_1 + r_2 = 100 + 181 = 281 \text{ pm}$

$$U_L = \frac{(1.214 \times 10^5) \times 3 \times 2 \times 1}{281} \left[1 - \frac{34.5}{281} \right]$$

$$= 2270 \text{ kJ mol}^{-1}$$

2.3 Born–Haber Cycles

Since energy is always conserved, the application of the First Law of Thermodynamics means that the change in enthalpy for a process does not depend on the way the energy change is carried out (this is often quoted as Hess's law). In 1919, Born¹ and Haber² working independently applied the First Law of Thermodynamics to the formation of ionic solids from their elements (*e.g.* Figure 2.5, for a simple binary ionic solid, A^+B^-). To calculate an unknown quantity is therefore just a matter of following the arrows in the cycle, provided all other values are known and the correct *sign* is used for each value (+ for *endothermic* processes and – for *exothermic*).

It should be noted that thermochemical cycles are often calculated at 298 K, whereas the energy terms such as electron affinity or ionization energy are defined at 0 K. Therefore, the values calculated by thermochemical cycles have an error of approximately 2–5 kJ mol^{-1} .

In Figure 2.5, each side of the cycle can be considered, so for energy to be conserved

$$-A + B + C + D = F - E$$

or

$$-A + B + C + D + E - F = 0$$

In addition to the lattice energy, electron affinity and ionization energy which have already been defined in this chapter, Born–Haber cycles also contain other quantities which allow for the fact, for example, that metals are not in the gaseous state at 298 K and that the halogens do not exist as mononuclear species.

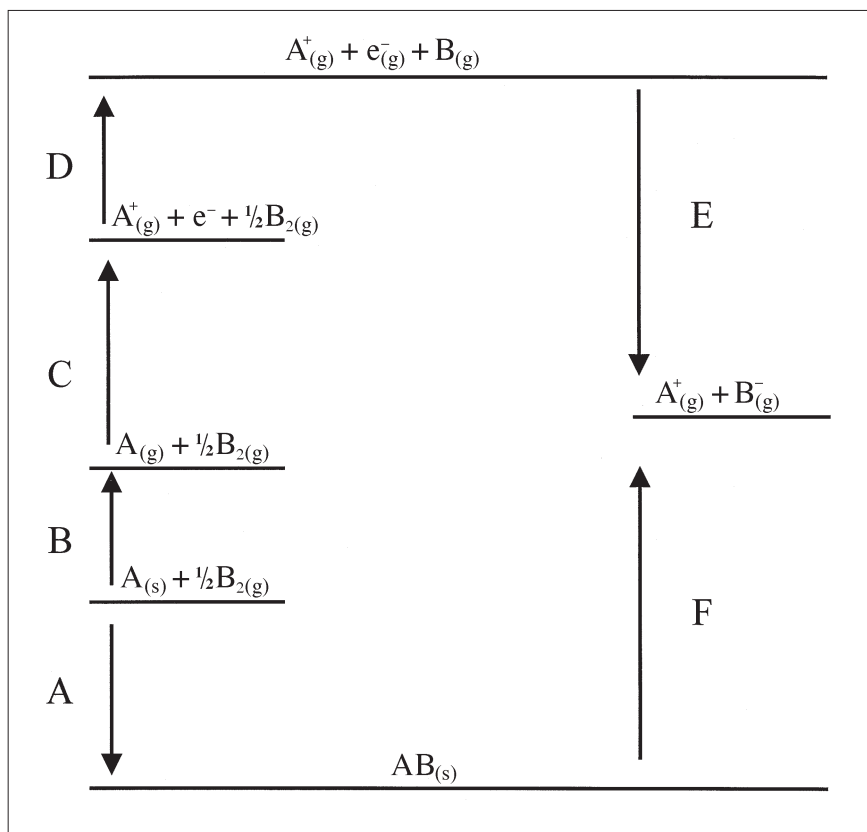
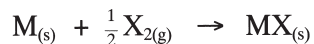


Figure 2.5 Born–Haber cycle for the formation for a Group 1 halide

2.3.1 Enthalpy of Formation, ΔH_f

The enthalpy change required to produce one mole of any compound from its constituent elements in their standard state



is called the **enthalpy of formation** for that compound. From Figure 2.5, the first stage (A) is formation of the elements in their standard state *from the ionic lattice*, *i.e.* $-\Delta H_f$.

A general method is being introduced here, in which enthalpies rather than free energies are being considered. However, the energetics of lattice formation is governed by the equation for Gibbs free energy, *i.e.*

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

where ΔG is the Gibbs free energy change, ΔH is the enthalpy change and ΔS is the entropy change during the reaction. A negative value of ΔG (energy given out during the process) indicates a lower

energy state of the system after the reaction and hence reaction is favoured.

The formation of a lattice from its gaseous ions is, however, very exothermic (ΔH is negative) so the loss in entropy is of negligible importance. The thermodynamic properties of crystal lattices therefore focus on changes in enthalpies rather than in free energies.

2.3.2 Enthalpy of Sublimation, ΔH_{sub}

The formation of one mole of gaseous atoms from one mole of the atoms in the standard state of the element



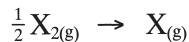
is called the **enthalpy of sublimation**, as in stage B.

2.3.3 Dissociation Enthalpy, ΔH_{diss}

In many cases, element B will exist as a diatomic molecule in its standard state (*e.g.* the halogens). To include it in the cycle the element must be dissociated to form monoatomic atoms, as in stage C:



Since we only have a singular X atom in the cycle we only need *one half of the dissociation enthalpy* in order to have one mole of X atoms. This value, for an element such as chlorine which normally exists as a diatomic molecule, is often known as the enthalpy of atomization, ΔH_{at} . This process is represented as:



If X is a Group 16 element (chalcogenide), *e.g.* sulfur, instead of a halogen, then the vaporization of the solid sulfur to the gaseous sulfur would have to be included in the cycle instead of ΔH_{diss} .

Stage D is the change in internal energy for the electron transfer to the non-metal element ($-E_a$) and stage E is the lattice enthalpy as previously defined.

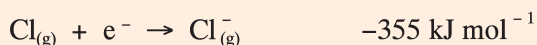
This whole cycle can be summarized as:

$$\Delta H = \Delta H(\text{atomisation}) + \Delta H(\text{ionisation}) - \Delta H_f$$

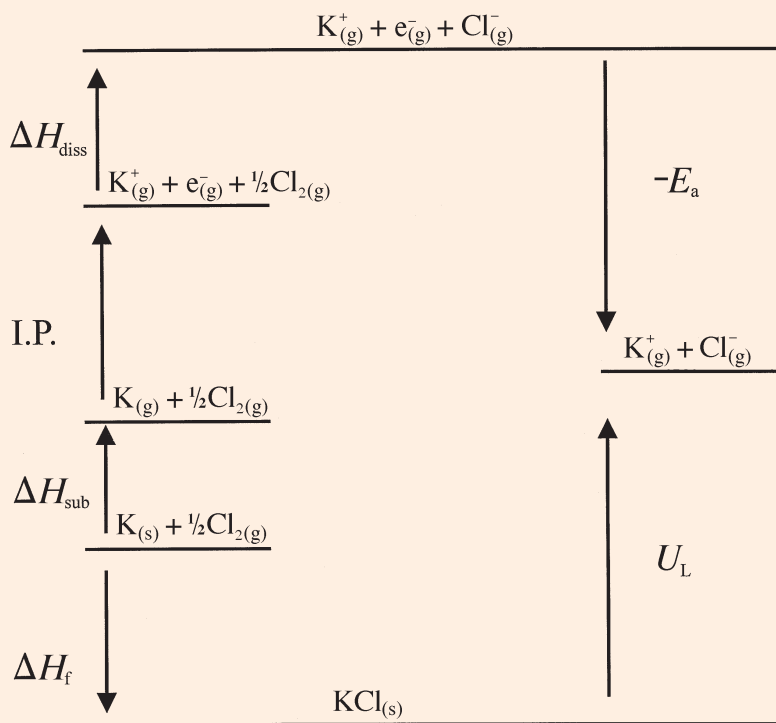
If any five of the quantities A–F are known, the sixth can be calculated.

Worked Problem

Q Use the data below to construct a thermochemical cycle for the formation of potassium chloride from its elements and hence calculate the lattice energy of potassium chloride.



A See Figure 2.6.



$$U_L = 89 + 425 + 244 - 355 + 438 = +719 \text{ kJ mol}^{-1}$$

This value is in good agreement with the experimental lattice energy of 709 kJ mol^{-1} , which strongly suggests that the ionic model is valid for potassium chloride.

Figure 2.6 Born-Haber cycle for the formation of KCl

Some caution should be applied when using data of this kind to predict the stability of compounds. The routes under which those compounds can decompose should be considered. For example, calculation of a lattice energy for the theoretical compound $\text{CaCl}_{(s)}$ produces an exothermic enthalpy of formation of approximately -200 kJ mol^{-1} . The compound CaCl ought therefore to exist. Chemical knowledge dictates that this compound does not exist. The reason becomes apparent by considering the equation:



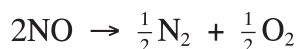
This reaction is more exothermic, with an enthalpy change of more than -600 kJ mol^{-1} . Any CaCl which might be formed disproportionates: the Ca^+ species become Ca^{2+} and Ca^0 .

2.4 Bond Enthalpies and Stability

In understanding the chemistry of the main group elements, an appreciation of the factors which affect the stability of compounds is paramount. Just as lattice energies can be used to predict stabilities of ionic lattices, **bond enthalpies** can be used to explain wide-ranging variations in the properties of the main group elements. For example, the differences in the physical and chemical properties of the dioxides of carbon and silicon can be explained by considering bond enthalpy terms. Similarly, why CH_4 is a very stable compound while PbH_4 is extremely unstable can be explained. In addition, other trends which occur in the chemistry of the main group elements can be understood in terms of simple energetics.

2.4.1 Stability and Instability; Kinetic and Thermodynamic Stability

In order to define the stability of an inorganic material we need to be precise about what we mean by stability. For example, CaCl_2 could conceivably decompose to a range of known or hypothetical compounds, *e.g.* to $\text{Ca} + \text{Cl}_2$, or to $\text{CaCl} + \frac{1}{2}\text{Cl}_2$, or to $\text{CaCl}_3 + 2\text{Ca}$. All of these routes would involve a large increase in the free energy of the system. We can therefore describe CaCl_2 as being *thermodynamically stable* with respect to other calcium chlorides/calcium/chlorine. A compound may be thermodynamically unstable, but *kinetically stable*, *i.e.* it has a negative free energy with respect to all possible decomposition products. For example, a sample of NO in a sealed container at room temperature does not decompose. However, the free energy change for the reaction



is -87 kJ mol^{-1} , indicating that NO is thermally unstable with respect to its constituent elements. Therefore, NO can be referred to as being *kinetically stable*; it is unstable in terms of energy, but the rate at which the change occurs at room temperature is so slow as to be undetectable. However, if NO is exposed to air, reaction with oxygen takes place to produce NO_2 . NO is therefore not stable in air, *i.e.* with respect to oxidation.

In conclusion, when referring to the stability of a compound one must be *precise*. Many inorganic compounds can be prepared which are thermodynamically unstable but kinetically stable with respect to decomposition along various routes. In addition, inorganic compounds which react with oxygen or water can often be handled in inert atmospheres, where they can be regarded as perfectly stable.

2.5 Bond Dissociation Energies and Bond Enthalpy Terms

Before any discussion about the application of bond enthalpy terms, it is important to check the definitions of **bond dissociation energies** and **bond enthalpy terms**.

The bond dissociation energy is defined as the enthalpy change associated with the reaction in which one mole of bond is *homolytically* broken, reactants and products being in the ideal gas state at 1 atm and 298 K.

Thus for methane, the bond dissociation energy for the first C–H bond is the energy change for the process:



This bond dissociation energy is specific to the reaction above, *i.e.* the energy for this C–H bond-breaking process depends on factors such as the other atoms attached to the carbon atom and the geometry of CH_4 and CH_3 . For example, if the remaining C–H bonds in methane are broken:



While bond dissociation energies are important in terms of the general understanding of physical chemistry, they are of little general use in predicting the stability of inorganic compounds, as they cannot be transferred between compounds.

Bond enthalpy terms, on the other hand, are quantities assigned to *each bond* in a molecule such that the sum over all bonds is equal to the enthalpy change associated with the conversion of the molecule into separate atoms. Bond enthalpy terms are assumed to be *constant*, and therefore transferable from molecule to molecule. So for methane:



so that the bond enthalpy term $B(\text{C-H})$ is $\frac{1}{4}\Delta H = 416 \text{ kJ mol}^{-1}$, *i.e.* the *average* for the four C-H bonds in CH_4 .

Bond enthalpy terms are not precise, particularly where there are changes in bond valency. For example, the value for C=C is $+612 \text{ kJ mol}^{-1}$, which is considerably less than twice the value for C-C. The values for $B(\text{C-H})$ and $B(\text{C-C})$, typically given in the literature as $+413 \text{ kJ mol}^{-1}$ and 347 kJ mol^{-1} , respectively, are good for working out the enthalpies of formation of a wide range of alkane hydrocarbons. This is because carbon always forms four covalent tetrahedral bonds in these compounds. For many inorganic systems, the valency of a particular element can vary markedly, and with it the number of bonds and the geometrical distribution of those bonds. For example, consider ClF_3 and ClF . The bond enthalpy terms for the Cl-F bond, derived from the enthalpies of formation of these compounds, are very different at $+174$ and $+255 \text{ kJ mol}^{-1}$, respectively. This demonstrates that transporting a chlorine-fluorine bond enthalpy term from one oxidation state of chlorine to another would produce considerable errors. Therefore, bond enthalpy terms are a useful guide, but their use should be treated with caution.

Some homolytic (between the same element) and heterolytic (between different elements) bond enthalpies are summarized in Table 2.4.

2.5.1 Variations in Bond Enthalpy Terms down a Main Group

Some general trends in bond enthalpies down a main group can be noted from Table 2.4. In Groups 14, 15, 16 and 17, if the element in the period from Li to F is A_1 , the period Na to Cl is A_2 , etc., then

1. In any vertical group A_1, A_2 , etc., the bond enthalpy $B(\text{A-X})$ diminishes down the group (A_1 to A_n) provided there are no lone pairs on X (*e.g.* H, C, but *not* N, O or F). So, for example, we have the data in Table 2.4 for the hydrides (A-H).
2. When there are lone pairs on X, the bond enthalpy order is usually:

$$B(\text{A}_1\text{-X}) < B(\text{A}_2\text{-X}) > B(\text{A}_3\text{-X}) > B(\text{A}_4\text{-X})$$

Table 2.4 Selected homolytic and heterolytic bond enthalpies (kJ mol^{-1})³⁻⁷

<i>Homolytic bond enthalpies</i>						
H-H						
432						
Li-Li	Be-Be	B-B	C-C	N-N	O-O	F-F
205	208	293	346	167	142	158
Na-Na	Mg-Mg	Al-Al	Si-Si	P-P	S-S	Cl-Cl
72	129	183	222	201	226	249
K-K	Ca-Ca	Ga-Ga	Ge-Ge	As-As	Se-Se	1Br-Br
49	105	115	188	146	72	190
Rb-Rb	Sr-Sr	In-In	Sn-Sn	Sb-Sb	Te-Te	I-I
45	84	100	146	121	126	149
<i>Heterolytic bond enthalpies</i>						
	A-H	A-F	A-Cl	A-Br	A-O	A=O
C	411	485	346	290	358	736
Si	318	565	381	310	466	638
Ge	285	452	349	276	385	-
N	386	313	283	-	201	607
P	322	490	322	263	335	544
As	247	406	309	256	301	389
Sb	-	402	314	264	-	-
O	459	190	218	201	144	498
S	364	284	255	217	468	-
Se	276	303	251	201	-	-
F	565	158	249	248	190	-
Cl	428	249	240	216	218	-
Br	362	248	216	190	201	-
I	295	278	210	177	201	-

Trend (1) is reasonably expected. As we proceed down a group, for example from carbon to lead, the atoms get larger and the orbitals involved in the bond have a more diffuse electron cloud, a poorer overlap with orbitals of X and thus form weaker bonds.

Trend (2) is more complex, but two factors contribute to inversion of the stability of A_1-X and A_2-X . One factor is repulsion between non-bonding electrons. The F-F bond is much weaker than the Cl-Cl bond for this reason. The non-bonding pairs for fluorine lie much closer to the nucleus and thus closer to the non-bonding pairs on the other nucleus, causing more repulsion and weakening the F-F bond relative to the Cl-Cl bond. The second factor is the possibility of d-orbital involvement in π -bonding for second-row elements. The second-row elements have vacant low-lying d-orbitals which can form a $d\pi-p\pi$ interaction with

p-orbitals on X, which are normally filled. This acts to strengthen the bond from the second-row element to X (where X has lone pairs), and helps account for trend (2). Such $d\pi-p\pi$ bonding can occur for heavier elements in a group, but since the orbitals are larger and the interaction is spread out over a larger volume, it will be a weaker effect.

Application of trends (1) and (2) can explain some obvious differences between chemical reactivity and structure in the main groups.

Double and Single Bonds

A major difference in the chemistries of first- and second-row elements is apparent in the relative stability of compounds with double and single bonds. Carbon-carbon double bonds are well known, whereas only recently have compounds with silicon-silicon double bonds been synthesized. Such compounds readily react to form other compounds in which the double bond is broken.

Worked Problem

Q Figure 2.7 shows the formation of four M–O single bonds from two M=O double bonds, where M = Si and C. Consider the enthalpy change for this reaction, and hence predict the preferred form of the oxide for each of Si and C.



A Using the data in the Table 2.4, we find:

For carbon $(736 \times 2 - 358 \times 4) = +40 \text{ kJ mol}^{-1}$

For silicon $(638 \times 2 - 466 \times 4) = -588 \text{ kJ mol}^{-1}$

For carbon the reaction to form four single bonds from two double bonds would be endothermic (*i.e.* unfavourable) and hence CO_2 exists as discrete molecules. Silicon much prefers the structure with four single bonds and SiO_2 is an infinite lattice of vertex-linked SiO_4 tetrahedra. The reasons for the different structures can be rationalized by considering the bonding in them. C=O bonds are strong, presumably owing to the good $p\pi-p\pi$ overlap which comes from the similar sizes of the oxygen and carbon p-orbitals and the short C–O distance. For Si=O, the overlap will be much poorer with a

Figure 2.7 Formation of four single M–O bonds from the decomposition of two double M=O bonds

longer Si–O distance and 3p–2p orbitals involved. In contrast, the Si–O single bond is stronger than the C–O single bond owing to $d\pi-p\pi$ interactions.

Stability of Gaseous Halides AX_n and the Inert Pair Effect

Among the heavy post-transition metals there is a definite reluctance to exhibit the highest possible oxidation state. For example, boron is always trivalent, but thallium shows significant chemistry of the +1 oxidation state, leaving a pair of electrons coordinatively inert. This is known as the **inert pair effect**.

The reasons for the differences can be explained using bond enthalpies. As we have seen, the values of the first ionization energies fall as a group is descended. Bond enthalpies to a particular element also decrease.

For example, Table 2.5 contains the first four ionization energies for the Group 14 elements. There are only small differences between the ionization energies for silicon, which primarily forms compounds in the +4 oxidation state, and lead which forms both divalent (+2) and tetravalent (+4) compounds.

A better understanding of the occurrence of the inert pair effect can be observed by considering the tendency for the following reaction to proceed either in the solid or gas phase:



Consider the values, in kJ mol^{-1} , for the gas phase reaction in Table 2.6. Although all these values for the decomposition are endothermic, the trend to decreasing stability of the high-valent (+4) fluoride compared with the low-valent (+2) iodide can be clearly seen. This is due to

Table 2.5 Ionization energies for the Group 14 elements (kJ mol^{-1})

	<i>1st</i>	<i>2nd</i>	<i>3rd</i>	<i>4th</i>
C	1090	2350	4610	6220
Si	786	1580	3230	4360
Ge	762	1540	3300	4390
Sn	707	1410	2940	3930
Pb	716	1450	3080	4080

Table 2.6 Bond enthalpies for the Group 14 halides (kJ mol^{-1})

Element	Fluoride	Chloride	Bromide	Iodide
C	467	346	290	213
Si	565	381	310	234
Ge	452	349	276	211
Sn	414	323	272	205
Pb	331	243	201	142

longer bonds and more diffuse orbitals giving poorer overlap and weaker bonds. Hence, as a group is descended the bonds to X become weaker, and their formation does not compensate for the endothermic energy terms such as breaking the X–X bond and the electron promotion (hybridization) energies $s^2p \rightarrow (sp^2)^3$. It is also worth noting that, as more bonds form around an atom, each successive bond normally gets weaker. For example, the series:

	ClF	ClF ₃	ClF ₅	
$B(\text{Cl-F})$	+255	+174	+151	kJ mol^{-1}

So the weakening bonds as the group is descended is really the origin of the tendency of an element to form the $n - 2$ oxidation state.

Summary of Key Points

1. Structures formed from ions have specific properties which are related to their geometrical structure, such as high melting point, brittle nature and localized electrons.
2. The actual assembly of positive and negative ions revealed by the X-ray diffraction technique shows sound agreement with theoretical mathematical expressions, in which ions are considered point charges. This allows the stability of purely theoretical ionic structures, *e.g.* CaCl or CaCl_3 , to be predicted.
3. Energy terms such as ionization energies and lattice energies (defined at 0 K) can be used in Born–Haber cycles to estimate unknown quantities under standard conditions.
4. Bond enthalpy terms can be used to explain differences in the

reactivity and bond strengths of the main group elements and to explain general trends such as the inert pair effect and the tendency to form double or single bonds.

Further Reading

- D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press, Cambridge, 1981.
 W. E. Dascent, *Inorganic Energetics*, Penguin, London, 1970.
 J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry*, 4th edn., Harper/Collins, New York, 1994.

Problems

- (i) Given that the cell parameter for calcium oxide, which crystallizes with the sodium chloride structure, is 483 pm, calculate the lattice energy for CaO.

(ii) Using the following data and the lattice energy calculated in part (i), construct a thermochemical cycle for the formation of calcium oxide from its elements and hence calculate the enthalpy of formation of CaO_(s):

$$\Delta H_{\text{sub}} = +177; \text{ionization potentials: first} = +590; \text{second} = +1100; \Delta H_{\text{dis}} = +498; \text{first } E_{\text{a}} = 142; \text{second } E_{\text{a}} = -844 \text{ (kJ mol}^{-1}\text{)}$$

(iii) Why might you expect the answer calculated in (ii) to have an error of about 5 kJ mol⁻¹?

(iv) Why is the second ionization potential for calcium much greater than the first despite forming a stable closed-shell configuration?
- Given that strontium oxide crystallizes with the same structure as calcium oxide, use data tables to estimate the minimum cation/anion distance and hence determine the lattice energy for SrO.
- The compound FrF cannot be isolated owing to short half-life of Fr. Use the Kapustinskii equation to calculate an approximate lattice energy for FrF, given that the sum of the francium and fluorine ionic radii is 4.2 Å
- The experimentally determined lattice energy for rubidium chloride is 702 kJ mol⁻¹. Use the Born–Lande model to calculate the

lattice energy for RbCl, and hence confirm that RbCl fits the ionic model.

5. (i) A thermochemical cycle for the formation of the aluminium sub-halides is given in Figure 2.8. Write an expression for ΔH_{dec} in terms of the other quantities in the cycle.

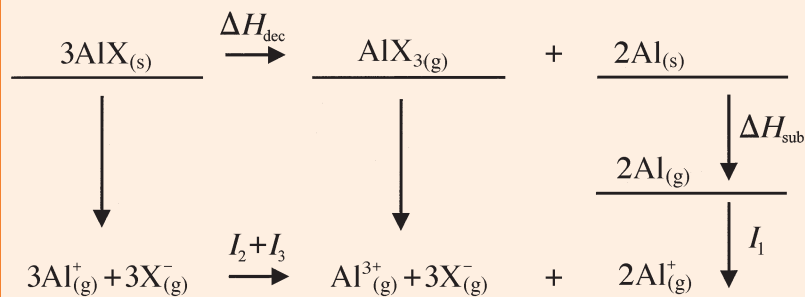


Figure 2.8 Thermochemical cycle for the formation of aluminium sub-halides

(ii) Assuming no entropy change, predict which oxidation state of aluminium is energetically favoured for the two halides, given the following data (kJ mol^{-1}):

$$\begin{array}{llll}
 I_1 = +577 & I_2 = +1816 & I_3 = +2743 & \Delta H_{\text{sub}} = +324 \\
 U(\text{AlF}) = +910 & & U(\text{AlI}) = +696 & \\
 U(\text{AlF}_3) = +6380 & & U(\text{AlI}_3) = +4706 &
 \end{array}$$

6. Explain the following observations.

- (i) The C–O single bond is weaker than the Si–O single bond whereas the double bonds show the reverse order of strength.
- (ii) The C–C bond and the F–F bonds are both considerably weaker than the C–F single bond.
- (iii) The N–N single bond is weaker than the P–P single bond.
- (iv) The Si–Cl bond is easily hydrolysed although the C–F bond is resistant to attack by water.

References

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3. T. L. Cottrell, *The Strength of Chemical Bonds*, Butterworth, London, 1958.
4. U. S. National Bureau of Standards, NSRDS-NBS 31, 1970.
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6. L. Brewer, *Chem. Rev.*, 1963, **63**, 111.
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