

3 Ionic interactions

In the previous chapter we saw how energy changes are crucial in determining whether or not a reaction will take place. There are two major sources of energy in chemical reactions: interactions between charged species (ions) and the making and breaking of covalent bonds. Ionic interactions are probably the easiest to understand so we will discuss these first before moving on to the more complex topic of covalent bonding. This chapter will only consider the interactions between ions in *solid* materials; ions in solution are of course very important in chemistry but are more complex to describe and so we will delay this until Chapter 12.

3.1 Ionic solids

That solid sodium chloride is made up of positively charged sodium ions and negatively charged chloride ions is such a familiar idea that we are perhaps in danger of taking it for granted, so we will spend a few moments reviewing the evidence for the existence of ions in such solid materials.

The best evidence comes from X-ray diffraction studies which can both locate the positions of the nuclei and also map the electron density between them. Such studies show that the sodium and the chlorine atoms are arranged in a regular lattice, as depicted in Fig. 3.1, and that the charge on the chlorine and sodium atoms is close to one unit. Furthermore, it is found that between adjacent sodium and chlorine nuclei the electron density falls to a very low value. These observations are consistent with the almost complete transfer of an electron from sodium to chlorine, leading to the formation of ions with little electron density between them.

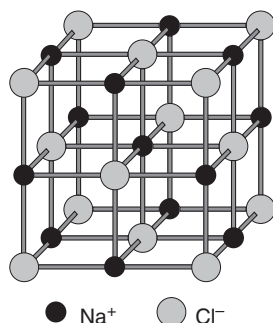


Fig. 3.1 Representation of part of the lattice of solid NaCl as determined by X-ray diffraction.

X-ray diffraction studies also allow us to measure the distances, $r(\text{MX})$, between the ions in the lattice. If we look at this data for the series of salts MBr and MCl, where M is any of the Group I metals (Li, Na, K, Rb, Cs), we find that the difference $r(\text{MBr}) - r(\text{MCl})$ varies by only a few percent as we change M. Similarly, if we look at the difference $r(\text{RbX}) - r(\text{KX})$, where X is one of the halogens, there is little variation from halogen to halogen.

These observations lead to the idea that each ion can be assigned an *ionic radius* which is more or less independent of the salt in which the ion is present. So, for example, the Na–Cl distance can be found by adding together the ionic radii of Na^+ and Cl^- ; the same value of the ionic radius of Cl^- can be used to find the K–Cl distance in solid KCl. That tables of such ionic radii can be drawn up suggest that, to a large extent, the ions can be thought of as behaving independently in the solid.

There are some physical properties which are often taken as being indicative of the presence of ions in a solid. For example, such solids are generally insulators but, on melting, the electrical conductivity rises sharply; this is at-

tributed to the ions being immobile in the solid but free to move in the liquid.

The energy of interaction between charged species, such as ions, has a simple form and we will be able to exploit this in the next section to develop a straightforward expression for the total energy of the ions in a lattice. We will then go on to see how this expression can be used to understand the energetics of the formation of a lattice and rationalize the outcome of some reactions involving solids.

3.2 Electrostatic interactions

In this section we are going to calculate the energy of interaction between the ions in a lattice just by considering the ions as charged objects. As you know, oppositely charged objects attract one another – that is there is a *force* between them; we call this the *electrostatic* or *Coulomb* interaction. This force is found to be proportional to the charges involved and inversely proportional to the square of the distance, r , between the two charges. The force is given by

$$\text{force} = \frac{q_1 q_2}{4\pi \epsilon_0 r^2}$$

where q_1 and q_2 are the two charges (in units of Coulombs), and ϵ_0 is a fundamental constant called the vacuum permittivity (it has the value $8.854 \times 10^{-12} \text{ F m}^{-1}$).

The *energy* of interaction of two charges, which is what we are interested in, is given by

$$\text{energy} = \frac{q_1 q_2}{4\pi \epsilon_0 r}, \quad (3.1)$$

which is properly described as the electrostatic (or Coulomb) potential energy. Note that it varies inversely with the distance in contrast to the force which varies as the inverse square of the distance.

The charge on an ion can be thought of as the result of an atom gaining or losing a whole number of electrons, which means that the charge can be expressed as a multiple of the charge on the electron, e (which is $1.602 \times 10^{-19} \text{ C}$). So for a singly charged negative ion the charge is $-e$, for a doubly charged negative ion the charge is $-2e$ and so on. Similarly, singly and doubly charged positive ions have charges of $+e$ and $+2e$, respectively.

We need to be careful to distinguish the *numerical* charge on the ion, which is an integer, and the actual charge on the ion, which is some multiple of e . The numerical charge of a positive ion will be written as z_+ and that of a negative ion as z_- ; z_+ and z_- are *always* positive numbers, even for negatively charged ions. The charge on a positive ion is z_+e and on a negative ion is $-z_-e$; note the introduction of the minus sign for the negatively charged species.

Putting these values for the charges q_1 and q_2 into Eq. 3.1, the energy of interaction of a positive and negative ion with numerical charges z_+ and z_- , respectively, is

$$\text{energy} = -\frac{z_+ z_- e^2}{4\pi \epsilon_0 r}. \quad (3.2)$$

The expression is *negative*, indicating that there is a *lowering* of the energy due to this favourable interaction between opposite charges.

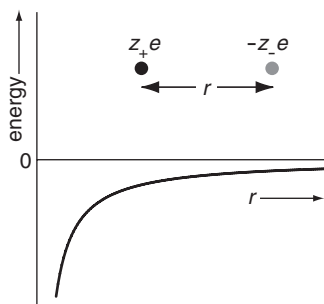
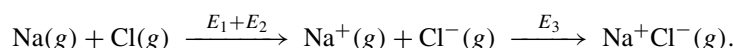


Fig. 3.2 Plot showing how the energy of interaction of two opposite charges varies with the distance between them. The energy is negative as the interaction is favourable, and the closer the ions are to one another the more negative the energy becomes.

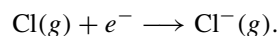
Figure 3.2 shows a plot of this energy as a function of the distance between the charges; the closer the two charges come, the more negative the energy. At large values of r the energy goes to zero, but on account of the $1/r$ dependence, this approach to zero is rather slow. The graph shows us that two oppositely charged ions will move towards each other, if they are able to, since this will lead to a lowering in the energy. We will now use this expression to discuss the energetics of the formation of an ion pair.

Forming an ion pair

Imagine we have sodium and chlorine *atoms* in the gas phase. Given what we know about these two elements, we might reasonably expect the sodium to lose an electron to form Na^+ and the chlorine to pick this electron up to form Cl^- . The two oppositely charged ions would then be attracted to one another, and so might form an NaCl molecule which we imagine to be an ion pair, Na^+Cl^- . The whole process can be written:



E_1 is the ionization energy of sodium, and has the value 502 kJ mol^{-1} ; E_2 is the electron affinity of chlorine, which is the energy of the process



The value of the electron affinity is -355 kJ mol^{-1} , so $E_1 + E_2$ is 147 kJ mol^{-1} . The fact that $E_1 + E_2$ is positive tells us that when a sodium and chlorine atom are far apart it is not favourable simply to remove an electron from the sodium and add it to the chlorine.

However, when the two oppositely charged ions come together there is a favourable energy of interaction, as shown by Fig. 3.2 – this means that E_3 will be negative. The closer the ions come together the more negative E_3 will become, eventually cancelling out the 147 kJ mol^{-1} (which is $E_1 + E_2$) and so making the overall process exothermic.

The usual expectation for molecules is that there will be a particular distance, the equilibrium distance, at which the energy of interaction is a minimum. However, this will not be the case for these two ions experiencing a Coulomb interaction; all that happens to them is that the energy goes on and on decreasing as the ions approach – there will be no minimum in the energy, which is simply not a realistic situation.

What is missing from our model is that at short enough separations even ions of opposite charge will begin to repel one another due to interactions between their electrons. This repulsive interaction is much shorter range than the Coulomb interaction and typically varies inversely as some high power of r :

$$\text{repulsion energy} \propto \frac{1}{r^n}$$

where n is between 5 and 12; it is around 8 for Na and Cl.

So what we have is a balance between the electrostatic interaction which makes the energy more negative as the ions get closer, and this repulsive interaction which makes the energy increase. The result is that there will be some

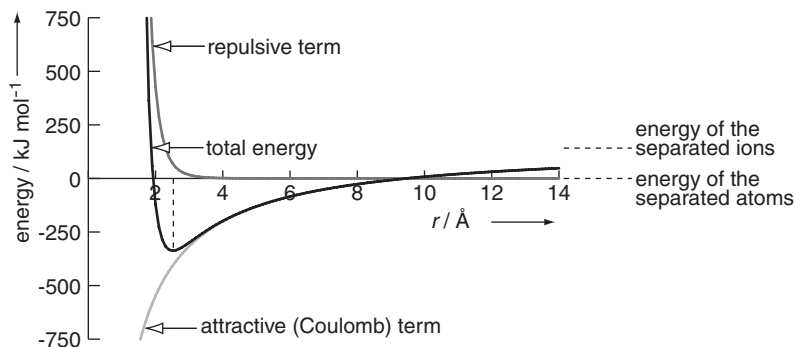


Fig. 3.3 Plot showing the different contributions to the energy of an Na^+Cl^- ion pair as a function of the distance between the two ions. The attractive Coulomb term is always negative and becomes increasingly so as the distance decreases. In contrast, the repulsive term is only significant at much shorter internuclear distances. Adding together these two contributions results in a total energy curve which has a minimum at around 2.5 Å, shown by the dashed line. Zero on the energy scale is defined as the energy of the two separated *atoms*. Since we are considering the interaction of two *ions* the energy at very large separations tends to 147 kJ mol^{-1} (shown by the dashed line) which, as was calculated on p. 22, is the energy needed to form the ions from the atoms.

distance at which the total energy is a minimum; this will be the equilibrium separation of the two ions. These points are illustrated in Fig. 3.3 which shows how the attractive Coulomb term, the repulsive term and the total energy vary with internuclear distance for the Na^+Cl^- pair.

As noted before, the Coulomb term is always negative and falls as the internuclear separation decreases. The repulsive term is much shorter range and, for this ion pair, only makes a significant contribution when the distance is less than about 3 Å; however, once it does get going it rises very steeply. Looking at the curve for the total energy we see that at large distances it follows the attractive Coulomb curve and falls as the distance decreases. Then, once the repulsive term starts to become significant the fall is slowed and eventually reversed leading to the formation of a minimum at around 2.5 Å; this corresponds to the equilibrium separation of the ion pair.

From the graph we can see that forming the ion pair from the atoms is significantly exothermic and so, although the entropy change is likely to be unfavourable, we can expect that the reaction will go. Our simple electrostatic model therefore accounts very nicely for the formation of NaCl molecules in the gas phase as ion pairs. However, this was not really what we set out to do – we are trying to work out the energy of a solid lattice – but as we will see in the next section, this can be done by quite a simple modification of the ion pair case.

Forming a lattice

In a lattice there are many ion–ion interactions which we need to take into account if we are going to estimate the energy using this model. However, as the ions are in a regular array it turns out not to be too difficult to work out what the total electrostatic energy is.

Look at the NaCl lattice depicted in Fig. 3.4 and concentrate on the Na^+ ion at the very centre, which is shown cross-hatched. Its closest neighbours, at a distance r_0 , are six Cl^- ions arranged at the corners of an octahedron. The

$$1 \text{ \AA (Ångström)} = 10^{-10} \text{ m or } 100 \text{ pm.}$$

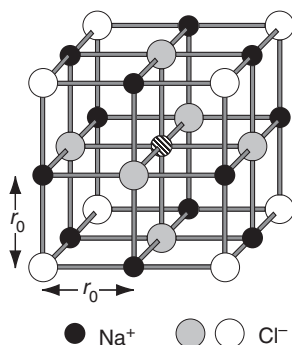


Fig. 3.4 Part of the lattice of solid NaCl. The closest neighbours of the central Na⁺ (shown cross-hatched) are the six Cl⁻ ions shown in grey, next are the 12 Na⁺ ions shown in black and next after that are the eight Cl⁻ ions shown in white. The distances between all of these ions and the central Na⁺ can be expressed in terms of the separation, r_0 , of adjacent ions.

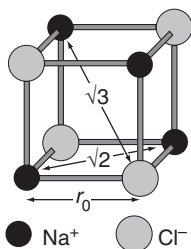


Fig. 3.5 Part of the lattice of NaCl showing how the distances can all be expressed in terms of the distance, r_0 , between adjacent ions. The closest distance between Na⁺ ions is across the diagonal of a square of side r_0 , giving a distance of $\sqrt{2}r_0$. The distance between Na⁺ ions and Cl⁻ ions which are at opposite corners of a cube is the length of the body diagonal, which is $\sqrt{3}r_0$.

energy that these six interactions contribute is just six times that of an ion pair separated by r_0 :

$$-6 \times \left(\frac{z_+ z_- e^2}{4\pi \epsilon_0 r_0} \right).$$

The next nearest neighbours are 12 Na⁺ ions, shown in black; these are at the opposite corner of a square to the central Na⁺ and so are at distance $\sqrt{2}r_0$ (see Fig. 3.5). As these ions are positive their interaction with the central Na⁺ leads to an increase in the energy (i.e. it is a repulsive interaction), so the term we have to add is positive:

$$\underbrace{-6 \times \left(\frac{z_+ z_- e^2}{4\pi \epsilon_0 r_0} \right)}_{\text{interaction with six Cl}^- \text{ at } r_0} \quad + \quad \underbrace{+12 \times \left(\frac{z_+ z_- e^2}{4\pi \epsilon_0 \sqrt{2}r_0} \right)}_{\text{interaction with 12 Na}^+ \text{ at } \sqrt{2}r_0}.$$

The next set of ions are the eight Cl⁻, and these are across the body diagonal from the central Na⁺ and so the separation is $\sqrt{3}r_0$. These ions are opposite in charge to the central ion and so contribute a negative term to the energy:

$$\underbrace{-6 \times \left(\frac{z_+ z_- e^2}{4\pi \epsilon_0 r_0} \right)}_{\text{interaction with six Cl}^- \text{ at } r_0} \quad + \quad \underbrace{+12 \times \left(\frac{z_+ z_- e^2}{4\pi \epsilon_0 \sqrt{2}r_0} \right)}_{\text{interaction with 12 Na}^+ \text{ at } \sqrt{2}r_0} \quad - \quad \underbrace{8 \times \left(\frac{z_+ z_- e^2}{4\pi \epsilon_0 \sqrt{3}r_0} \right)}_{\text{interaction with eight Cl}^- \text{ at } \sqrt{3}r_0}.$$

We can tidy this expression up by taking out the common factor:

$$\text{electrostatic energy} = -\frac{z_+ z_- e^2}{4\pi \epsilon_0 r_0} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} + \dots \right) \quad (3.3)$$

where the ... indicate that we can go on adding more terms as we move further away from the central ion. The series in the bracket in Eq. 3.3 turns out, after many terms, to converge on a value of 1.748.

This number is called the *Madelung constant*, M , and is characteristic of the particular arrangement of ions in the lattice; typical values of M are between 1.6 and 2.5. Using the value of M we can write the total electrostatic (Coulomb) energy as

$$\text{electrostatic energy} = -\frac{M N_A z_+ z_- e^2}{4\pi \epsilon_0 r}$$

where we have multiplied by Avogadro's number, N_A , so as to obtain the molar energy. Also, we have written the lattice spacing more generally as r , rather than as the equilibrium separation, r_0 .

As with the ion pair, we need to include a term to account for the repulsion between ions; writing this as $+B/r^n$ we have our final expression for the total energy as

$$\text{total energy} = -\frac{M N_A z_+ z_- e^2}{4\pi \epsilon_0 r} + \frac{B}{r^n}.$$

We do not know the value of the constant B , nor of the exponent, n . It turns out that the total energy is not particularly sensitive to the value of n so we

can safely set it at some reasonable value. A value for B can be found by recognizing that the energy must be a minimum at the equilibrium separation, r_0 (we will not go into the details here). The final expression for the energy of the lattice at the equilibrium separation is

$$\text{energy at equilibrium} = -\frac{MN_{\text{A}}z_+z_-e^2}{4\pi\epsilon_0r_0}\left(1 - \frac{1}{n}\right) \quad (3.4)$$

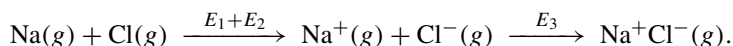
which is known as the *Born–Landé equation*.

The importance of the lattice

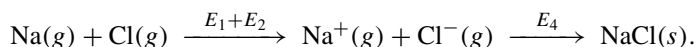
If instead of forming a lattice we form ion pairs, the energy would be given by Eq. 3.4 with M set to 1. This is because the only interaction is between ion pairs and so in Eq. 3.3 the quantity in the bracket will just be 1, representing the single interaction between oppositely charged ions.

For a lattice, M is greater than 1 which means that its formation is *more* energetically favourable than the formation of ion pairs. The reason for this is that in the lattice it is not just two ions which are interacting but many. True, some of the interactions in the lattice are between ions of like charge and so are repulsive, but on balance the favourable interactions between opposite charges win.

The example of forming Na^+Cl^- ion pairs which we discussed on p. 22 illustrates these points nicely:

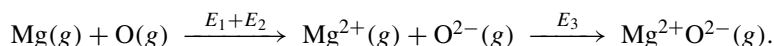


As explained before, $E_1 + E_2$ is 147 kJ mol^{-1} . If we assume that the bond length in Na^+Cl^- is the same as the equilibrium separation in the lattice (2.8 \AA) then we can use Eq. 3.4 with $M = 1$ to find $E_3 = -417 \text{ kJ mol}^{-1}$. These values make the overall process exothermic. However, if we allow a lattice to form:

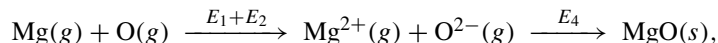


E_4 is greater in magnitude than E_3 by a factor of M (1.75) which is rather significant. So, forming the lattice is a much more exothermic process than forming the ion pairs.

The case of forming MgO shows up this difference even more dramatically:



Now $E_1 + E_2$ is 2807 kJ mol^{-1} and using an internuclear separation of 2.1 \AA we find E_3 is $-2266 \text{ kJ mol}^{-1}$. Thus, the process of forming the ion pairs is endothermic and so unlikely to be favourable. However, if we form a lattice rather than the ion pairs



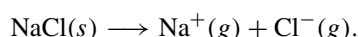
we find that E_4 is now $-3961 \text{ kJ mol}^{-1}$, making the overall process exothermic. So, forming ion pairs is endothermic, but forming the lattice is exothermic

– a nice illustration of the large extra lowering in energy to be had from forming the lattice.

We should end on a note of caution here. Species such as NaCl and MgO are known in the gas phase, but their internuclear separations are significantly less than the corresponding separations in the crystal. This is taken to imply that the bonding in these simple diatomics is not entirely ionic but has a significant covalent component.

3.3 Estimating lattice energies

The Born–Landé equation, Eq. 3.4, is an expression for the energy of interaction between the ions in a crystal lattice. Usually, when we are thinking about the energetics of solid lattices we talk in terms of the *lattice energy* which is the energy needed to take the ions from the lattice into the gas phase where they are so far apart that they are not interacting. For NaCl the process is



The energy of the ions in the lattice is given by Eq. 3.4 and as the gaseous ions are not interacting at all their electrostatic energy is zero. Hence the lattice energy is just minus the energy given by Eq. 3.4:

$$\text{lattice energy} = \frac{MN_{\text{A}}z_+z_-e^2}{4\pi\epsilon_0r_0} \left(1 - \frac{1}{n}\right). \quad (3.5)$$

Strictly speaking this expression gives the change in what is called the *internal energy*, rather than the enthalpy; what is more the energy is for a process taking place at 0 K. It is possible to correct the value to give the usual enthalpy change at 298 K, but the correction is small and not really of any significance for the calculations we are going to do here. We will simply use Eq. 3.5 as an expression for the lattice enthalpy, which is the enthalpy change of going from the solid to the gaseous ions.

Let us use Eq. 3.5 to estimate the lattice energy of NaCl. For this crystal the value of r_0 determined by X-ray diffraction is 2.81 Å, the appropriate value of n is 8 and, as already mentioned, the Madelung constant is 1.748. These data are all we need to compute the lattice energy as 754 kJ mol⁻¹, a value which compares very favourably with the accepted value of 773 kJ mol⁻¹. It is remarkable that this very simple model produces such a good estimate of the lattice energy.

A similar calculation for MgO ($r_0 = 2.00$ Å) gives the lattice energy as 4043 kJ mol⁻¹. This value is much larger than that for NaCl on account of the much stronger interactions between the doubly charged Mg²⁺ and O²⁻ ions in MgO. It is striking how large these lattice energies are, indicating that the interaction between ions is a very significant contributor to the energy changes in chemical processes.

Ionic radii

We mentioned right at the start of this chapter (p. 20) that in a crystal it is possible to assign a radius to each ion, the value of which is broadly independent of the lattice in which the ion is found. This is very useful to us as it means that we can compute the equilibrium separation, r_0 , needed in Eq. 3.5 as the sum of the radii of the positive and negative ions, r_+ and r_- , respectively:

$$r_0 = r_+ + r_-.$$

So, if we want to work out the lattice energy of a compound, rather than needing to know the value of r_0 (which would require X-ray diffraction experiments on the crystal) we can simply look up the ionic radii from tables. Some typical values of ionic radii (in units of Å) are shown in the table below:

cations				anions			
$z_+ = 1$		$z_+ = 2$		$z_- = 1$		$z_- = 2$	
Li ⁺	0.68	Mg ²⁺	0.68	F ⁻	1.33	O ²⁻	1.42
Na ⁺	1.00	Ca ²⁺	0.99	Cl ⁻	1.82	S ²⁻	1.84
K ⁺	1.33	Sr ²⁺	1.16	Br ⁻	1.98	Se ²⁻	1.97
Rb ⁺	1.47	Ba ²⁺	1.34	I ⁻	2.20	Te ²⁻	2.17

There are some general trends evident from this table:

- as we go down a group the radii increase;
- for elements in the same row of the Periodic Table, 2+ ions are smaller than 1+ ions;
- anions are generally larger than cations;
- for elements in the same row of the Periodic Table, 2- ions are larger than 1- ions.

It makes sense that 2+ ions are smaller than 1+ ions, as when an electron is removed the remaining electrons are held more tightly and so are pulled in by their attraction to the nucleus. Similarly, the increased size of anions is due to the electrons experiencing less attraction to the nucleus. In the following chapter we will look in more detail at the interactions which are responsible for these changes.

We should be aware of the limitations of such tables of ionic radii. Usually they have been ‘adjusted’ to give, on average, the best estimates of the lattice energy. Different people have different ideas of the best adjustments to make, so you will find that the values of ionic radii quoted in one book are often different to those quoted in another! For a particular lattice the value of r_0 determined by using these tabulated ionic radii is best regarded as a reasonable estimate, and so the value of the lattice energy we determine must be treated with caution. It will not be more precise than a few percent, at best.

The Kapustinskii equations

The Russian scientist A. F. Kapustinskii noticed that the ratio M/ν , where M is the Madelung constant and ν is the number of ions in the molecular formula, varied rather little from crystal structure to crystal structure. He proposed that a good compromise was to take the value for this ratio as 0.874, thus enabling the value of M to be written as 0.874ν . Kapustinskii also proposed that a typical value of $n = 9$ should be used in Eq. 3.5. With these two simplifications the expression for the lattice energy becomes:

$$\text{lattice energy} = \frac{0.874\nu N_A z_+ z_- e^2}{4\pi\epsilon_0(r_+ + r_-)} \left(1 - \frac{1}{9}\right)$$

where we have replaced r_0 by $(r_+ + r_-)$. Putting in the values of all the constants we find the following rather simple expression for the lattice energy

$$\text{lattice energy/ kJ mol}^{-1} = \frac{1070 \nu z_+ z_-}{(r_+ + r_-)} \quad (3.6)$$

where the ionic radii are in Å.

For NaCl there are two ions in the molecular formula, so $\nu = 2$; from tables we find the radius for Na^+ to be 1.00 Å and for Cl^- to be 1.82 Å. Putting these numbers into Eq. 3.6 gives us a value of the lattice energy of 759 kJ mol^{-1} , which is quite close to the accepted value.

Equation 3.6 makes it clear that the lattice energy is dominated by two things: the charges on the ions and the ionic radii. A large lattice energy will result if the charges on the ions are large or the ions small.

The Kapustinskii expression for the lattice energy is rather simple and we will find it very useful in the following examples. However, we should recognize that the values it gives will be quite approximate and so we must be cautious about interpreting the results of our calculations in too detailed a way.

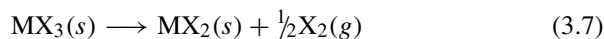
3.4 Applications

In this section we are going to look at two reactions in which trends can be understood using calculated lattice energies.

Stabilization of high oxidation states by fluorine

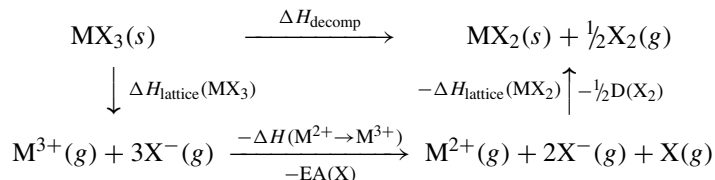
For many metals it has been observed that whereas the fluorides of high oxidation states are relatively easy to prepare, it is often the case that the other halides are more difficult or impossible to form. For example, CuF_2 is known, whereas attempts to prepare the corresponding copper (II) iodide have not been successful. Similarly, for cobalt in oxidation states III and IV, only the fluorides have been prepared. The story is similar for manganese where for oxidation state II all of the halides are known but for oxidation state III only the fluoride has been prepared. There are numerous other examples of this tendency of high oxidation states only to be found as the fluoride.

It is thought that the difficulty in preparing these high oxidation state halides comes about due to the tendency for the halide to decompose into the lower oxidation state with the release of the halogen. For the case of an oxidation state III metal the reaction we are talking about is



where M is the metal and X a halogen.

What we are going to do is to estimate the energy change for this reaction and see what effect changing the halogen has. The analysis will be done using the following cycle



Starting on the left the solid MX_3 is dissociated into its constituent ions in the gas phase: the energy needed is the lattice enthalpy of MX_3 . The M^{3+} ion then gains an electron from one of the X^{-} ions to give M^{2+} and an X atom: the energy needed is minus the third ionization energy of M, minus the electron affinity of X, $\text{EA}(\text{X})$. Finally, the M^{2+} and X^{-} ions are recombined to form solid MX_2 , for which the energy change is minus the lattice enthalpy of MX_2 , and the X atom recombines to form an X_2 molecule, for which the energy change is minus half the dissociation energy of X_2 , $D(\text{X}_2)$.

Overall, the enthalpy change for decomposition, ΔH_{decomp} , is

$$\begin{aligned} \Delta H_{\text{decomp}} = & \Delta H_{\text{lattice}}(\text{MX}_3) - \Delta H(\text{M}^{2+} \rightarrow \text{M}^{3+}) \\ & - \text{EA}(\text{X}) - \Delta H_{\text{lattice}}(\text{MX}_2) - \frac{1}{2}D(\text{X}_2). \end{aligned} \quad (3.8)$$

We can find the dissociation energies, ionization energies and electron affinities from tables. The lattice energies can be estimated using the Kapustinskii formula, Eq. 3.6. For MX_3 , the number of ions, ν , is 4, $z_+ = 3$ and $z_- = 1$, so the lattice energy is given by

$$\Delta H_{\text{lattice}}(\text{MX}_3) / \text{kJ mol}^{-1} = \frac{1070 \times 4 \times 3 \times 1}{(r_{\text{M}^{3+}} + r_{\text{X}^{-}})} = \frac{12840}{(r_{\text{M}^{3+}} + r_{\text{X}^{-}})}.$$

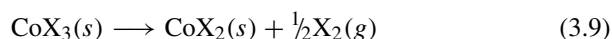
For MX_2 , $\nu = 3$, $z_+ = 2$ and $z_- = 1$, so the lattice energy is given by

$$\Delta H_{\text{lattice}}(\text{MX}_2) / \text{kJ mol}^{-1} = \frac{1070 \times 3 \times 2 \times 1}{(r_{\text{M}^{2+}} + r_{\text{X}^{-}})} = \frac{6420}{(r_{\text{M}^{2+}} + r_{\text{X}^{-}})}.$$

We will complete the calculation for the specific case of cobalt, for which the 3+ ion has a radius of 0.58 Å, and the 2+ ion a radius of 0.71 Å. These data enable us to compute the required lattice energies and thus we can complete the calculation for all the halogens as shown in the table below.

	F	Cl	Br	I
$r_{X^-} / \text{\AA}$	1.33	1.82	1.98	2.20
1 $\Delta H_{\text{lattice}}(\text{CoX}_3) / \text{kJ mol}^{-1}$	6723	5350	5016	4619
2 $\Delta H(\text{Co}^{2+} \rightarrow \text{Co}^{3+}) / \text{kJ mol}^{-1}$	3238	3238	3238	3238
3 $\text{EA}(X^-) / \text{kJ mol}^{-1}$	-334	-355	-331	-301
4 $\Delta H_{\text{lattice}}(\text{CoX}_2) / \text{kJ mol}^{-1}$	3147	2538	2387	2206
5 $\frac{1}{2}D(X_2) / \text{kJ mol}^{-1}$	79	121	112	107
6 $\Delta H_{\text{decomp}} / \text{kJ mol}^{-1}$	592	-192	-390	-631

In accordance with Eq. 3.8, the value on line 6 is computed by subtracting the values on lines 2 – 5 from that on line 1; these different contributions to ΔH_{decomp} are visualized in Fig. 3.6. We see clearly from the table that the decomposition reaction



is exothermic for all of the halogens except fluorine. This provides a neat explanation as to why it is possible to prepare CoF_3 but not any of the other trihalides as these can decompose to the lower oxidation state via an exothermic reaction.

In this reaction there is certainly an increase in the entropy as a gas is formed from solid reactants. However, this favourable entropy change is unlikely to outweigh the large positive enthalpy change in the case of the fluoride. For the other halogens, both the increase in entropy and the exothermicity imply that the reaction will go to products.

Just why it is that the fluoride is so different to the other halides can be appreciated by looking at Fig. 3.6. What the diagram shows is that in compar-

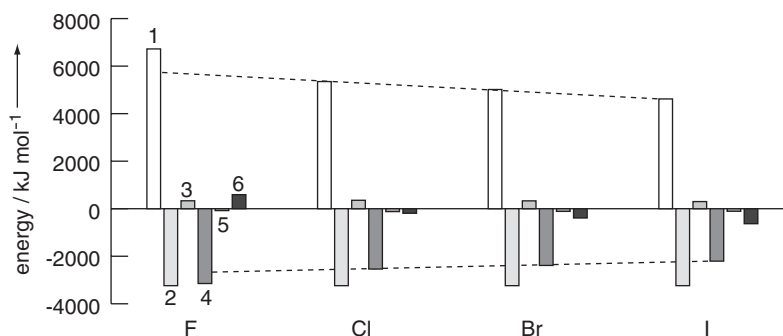


Fig. 3.6 Visualization of the different contributions to ΔH_{decomp} for the decomposition of CoX_3 according to Eq. 3.9. The bars indicate the size of the different energy terms given in the table above, with the numbers on the bars corresponding to the lines in the table. The quantities from lines 2 – 5 are plotted as minus the values shown in the table, as this is how they appear in the calculation of ΔH_{decomp} according to Eq. 3.8. Note how the lattice energies (numbered 1 and 4) and the ionization energy (numbered 2) are the dominant terms. The dashed lines show how the lattice energies of the chloride, bromide and iodide follow a steady trend, whereas the values for the fluoride are out of line with the others, being rather larger than the trend would suggest. It is this which makes the decomposition reaction for the fluoride endothermic.

ing one halide with another the lattice energies (lines 1 and 4 in the table) are the dominant terms (the ionization energy of the cobalt is significant, but is a constant for this series of compounds). We see that for the iodide, bromide and chloride there is a steady rise in the lattice energies which is simply due to the ions getting smaller. However, the increase in the lattice energy for the fluoride is much greater than the trend would suggest – something we can attribute to the unusually small size of the fluoride ion compared to the other halogens.

Figure 3.6 also shows us that as the halide ion gets smaller the increase in the lattice energy of CoX_3 is greater than for CoX_2 ; the different slopes of the dashed lines highlight this observation. It is easy to see why there is this difference by looking at the expressions for the lattice energies:

$$\Delta H_{\text{lattice}}(\text{CoX}_3) = \frac{12840}{(r_{\text{Co}^{3+}} + r_{\text{X}^-})},$$

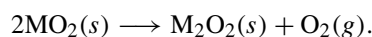
$$\Delta H_{\text{lattice}}(\text{CoX}_2) = \frac{6420}{(r_{\text{Co}^{2+}} + r_{\text{X}^-})}.$$

On account of the larger number in the numerator for CoX_3 , changing the radius of the negative ion will lead to a greater change in the lattice energy than for CoX_2 . So, when it comes to the fluoride the increase in the lattice energy is significantly greater for CoF_3 than for CoF_2 ; ultimately it is this large increase which tips the balance making the decomposition reaction endothermic for the fluoride.

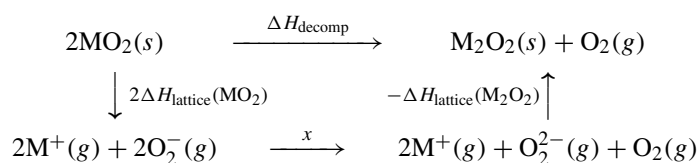
Peroxides and superoxides of the Group I metals

Our final example is concerned with the range of different compounds that are produced when Group I metals combine with oxygen. Lithium gives the simple oxide Li_2O , sodium gives mainly the peroxide, Na_2O_2 , and metals further down the group give mainly the superoxide MO_2 (the anion present in the peroxide is O_2^{2-} and in the superoxide the anion is O_2^-). The trend is for the metals with the larger ions to form the superoxide – an observation which we will be able to rationalize using lattice energies.

Let us consider the reaction in which the superoxide decomposes to the peroxide plus oxygen gas; this is presumably the reaction by which the superoxides of sodium and lithium would decompose, were they to be formed:



We can analyse this reaction using the following cycle:



The quantity simply denoted x is the enthalpy change on going from the superoxide anion to the peroxide anion plus gaseous O_2 ; for the present discussion we do not need to know its value.

The enthalpy change of the decomposition reaction, ΔH_{decomp} , can be computed from:

$$\Delta H_{\text{decomp}} = 2\Delta H_{\text{lattice}}(\text{MO}_2) + x - \Delta H_{\text{lattice}}(\text{M}_2\text{O}_2). \quad (3.10)$$

As before, we can use the Kapustinskii expression (Eq. 3.6 on p. 28) to estimate the lattice energies:

$$\begin{aligned} \Delta H_{\text{lattice}}(\text{MO}_2)/\text{kJ mol}^{-1} &= \frac{1070 \times 2 \times 1 \times 1}{(r_{\text{M}^+} + r_{\text{O}_2^-})} = \frac{2140}{(r_{\text{M}^+} + r_{\text{O}_2^-})} \\ \Delta H_{\text{lattice}}(\text{M}_2\text{O}_2)/\text{kJ mol}^{-1} &= \frac{1070 \times 3 \times 1 \times 2}{(r_{\text{M}^+} + r_{\text{O}_2^{2-}})} = \frac{6420}{(r_{\text{M}^+} + r_{\text{O}_2^{2-}})}. \end{aligned}$$

Substituting these expressions into Eq. 3.10 we have

$$\Delta H_{\text{decomp}} = \left[\underbrace{\frac{4280}{(r_{\text{M}^+} + r_{\text{O}_2^-})}}_{2\Delta H_{\text{lattice}}(\text{MO}_2)} - \underbrace{\frac{6420}{(r_{\text{M}^+} + r_{\text{O}_2^{2-}})}}_{\Delta H_{\text{lattice}}(\text{M}_2\text{O}_2)} \right] + x.$$

The radii of the O_2^{2-} and O_2^- ions are not that much different, so the quantity in the square bracket is negative on account of the larger numerator of the second fraction. Now imagine what happens as the size of the cation M^+ is increased; both lattice energy terms decrease but the one for M_2O_2 decreases more than the one for MO_2 on account of the larger numerator in the second fraction. The term in the bracket therefore becomes *less negative* as the radius of the metal ion increases.

We therefore conclude that the trend is for the decomposition reaction of the superoxide to become less favourable in energetic terms as the size of the metal ion increases. This rationalizes the observation that the superoxide is not found for the early members of Group I, but is found for the elements toward the bottom of the group which have the larger ions.

The argument here is not as detailed as in the previous example. We have not computed explicit values of the ΔH_{decomp} for the different metals and then compared them with one another. Rather, recognizing from the first example that the variation in the lattice energies is usually the crucial factor, we have simply looked at the way in which these terms will vary as the ionic radii are changed.

3.5 Ionic or covalent?

We mentioned at the start of this chapter that X-ray diffraction studies of crystals such as NaCl reveal that the electron density falls to a very low value between adjacent ions, and we cited this as evidence for the existence of ions in such crystals. However, if we look more closely at the electron density in ‘ionic’ solids such as LiF, NaCl and KCl we find two things. Firstly, although the density between ions of opposite charge does become very low it does not

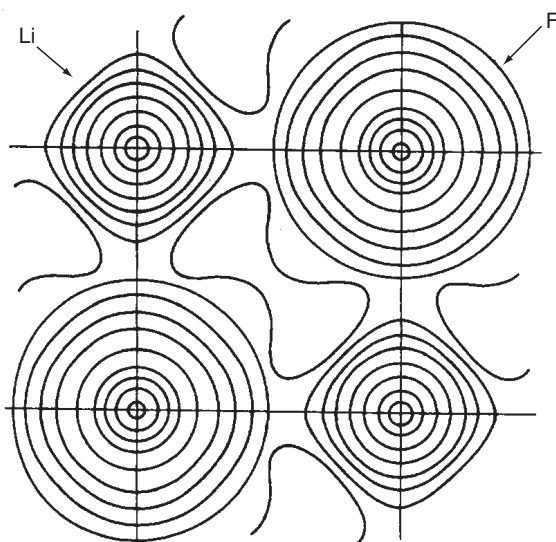


Fig. 3.7 Experimental electron density map for LiF determined using X-ray diffraction. The electron density is indicated by contours and the map shows the density in what would be a horizontal plane through the schematic structure shown in Fig. 3.1. Note that the electron distribution around the lithium is not spherical, which is taken as evidence of some covalent character in the bonding. (Reproduced, with permission, from H. Witte and W. Woelfel, *Reviews of Modern Physics*, **30**, 53, (1958). Copyright (1958) by the American Physical Society.)

actually fall to zero. Secondly, the distance between the nucleus and the minimum in the electron density does not correspond to the tabulated value of the ionic radius. These two observations cast doubt on whether these solids really do contain ions in the way we have assumed.

Close inspection of the electron density map, such as the one shown in Fig. 3.7 for LiF, reveals further problems. The contours of electron density around the lithium are not circular; if the lithium really was an ion its electron density would be spherical and so the contours would be circular. This distortion is taken as evidence that the lithium is not truly an ion but that there is some sharing of electrons with the fluorine – in other words there is some *covalent* contribution to the bonding.

Further evidence for there being some covalent contribution to the bonding in these apparently 'ionic' solids comes from comparison of the calculated and experimentally determined values of the lattice energies (remember that such energies can be determined experimentally using a Born–Haber cycle). Whereas compounds such as NaCl and KI show good agreement between the experimental and calculated values, for compounds of Ag(I) (e.g. AgI) and Tl(I) (e.g. TlBr) the experimental lattice energy is significantly in excess of the

calculated value. As the calculation only considers the electrostatic contribution, this discrepancy is taken as indicating the presence of additional covalent contributions.

In reality what we have is a continuum of types of bonding. At one extreme there is purely ionic bonding and at the other there is purely covalent bonding. Compounds such as LiF lie pretty close to the purely ionic end of the scale, whereas solids such as diamond and graphite are purely covalent. Everything else lies in between and so will have both covalent and ionic contributions to the bonding; which is dominant is sometimes quite hard to decide!

Unfortunately, all of this casts our lattice energy calculations into further doubt. However, we can continue to use these and to think about such solids as being 'ionic' provided that we realize that this is just an idealization and so treat our conclusions with some caution.

We now need to turn to the question of how to describe covalent bonding which, along with ionic interactions, is the other important source of energy in chemical reactions. As you know, it is the interactions between charged nuclei and electrons which are responsible for forming the covalent bonds which hold molecules together, so the first topic we must address is how to describe the behaviour of electrons in atoms and molecules. The next three chapters are devoted to this subject.