Lattice Enthalpy, Born–Haber and related enthalpy cycles

Ionic bonding revisited

Definition:	electrostatic attraction between oppositely charged ions.
Character:	ionic bonds are strong, so melting points of ionic compounds are high. The strength of ionic bonding is directly related to a quantity called the **enthalpy of lattice formation** (often reduced to **lattice enthalpy**) of the ionic compound.
$\Delta_{LE}H^{\ominus}$	The energy change when ONE MOLE of a solid ionic lattice is formed FROM ITS GASEOUS IONS under STANDARD CONDITIONS of 298K, 101kPa

As usual we can express this enthalpy change using a equation:

$\Delta_{LE}H^{\ominus}$ for potassium chloride: $K^+_{(g)} + Cl^-_{(g)} \rightarrow KCl_{(s)}$ = -711 kJ mol^{-1}

Key ideas

- Enthalpies of lattice formation are negative – energy is released when the ionic bonds are formed (just as conversely it takes energy to break bonds).
- Lattice enthalpies can't be measured directly (its impossible to form exactly one mole of ionic lattice from a collection of gaseous ions) but are very useful in order to understand the properties of ionic substances which relate to the strength of the lattice such as melting point and solubility in water.
- Molecules don't have lattice enthalpies – they are covelantly bonded and have no ions!

We have used Hess's law before in order to calculate energy changes we can't measure, and we'll use that technique again here in a diagram known as a BORN-HABER cycle, which brings together all the energy changes we need to know in order to work out $\Delta_{LE}H^{\ominus}$.

Relevant energy changes

We need to know these, be able to define them, and be able to write equations to represent them.

1) The enthalpy change of formation

$\Delta_f H^{\ominus}$ the enthalpy change associated with the formation of one mole of a substance from its elements in their standard states under standard conditions of 298K and 101kPa

The is usually an EXOTHERMIC process for an ionic compound.

e.g. $K_{(s)} + ½ Cl_{2(g)} \rightarrow KCl_{(s)}$ $\Delta_f H^{\ominus}$ = -437 kJ mol^{-1}

2) The enthalpy change of atomisation

$\Delta_{at}H^{\ominus}$ the enthalpy change when one mole of gaseous atoms is formed from the element in the standard state at 298K and 101kPa

This will be an ENDOTHERMIC process as energy is needed to break whatever bonds (metallic or covalent) hold the element together.

e.g. $K_{(s)} \rightarrow K_{(g)}$ $\Delta_{at}H^{\ominus} = +89\ \text{kJ mol}^{-1}$
$\frac{1}{2}\,Cl_{2(g)} \rightarrow Cl_{(g)}$ $\Delta_{at}H^{\ominus} = +121\ \text{kJ mol}^{-1}$

3) The first ionisation energy

$\Delta_{I1}H^{\ominus}$ the energy required to remove one electron from each atom in a mole of atoms of an element in the gaseous state to form gaseous ions with 1+ charge at 298K and 101kPa

This will be an ENDOTHERMIC process because the electron being removed has to overcome the attraction of the positively charged nucleus to escape
e.g. $K_{(g)} \rightarrow K^{+}_{(g)} + e^{-}$ $\Delta_{I1}H^{\ominus} = 419\ \text{kJ mol}^{-1}$

If we need to remove more electrons to form the positively charged ion from which the lattice is to be made, we'll need $\Delta_{I2}H^{\ominus}$ and so on.

$\Delta_{I2}H^{\ominus}$ is the energy required to remove one electron from each ion is a mole of gaseous ions of an element with 1+ charge, to make gaseous ions with 2+ charge at 298K and 101kPa. This will also be ENDOTHERMIC, as will subsequent $\Delta_{I}H^{\ominus}$

4) The first electron affinity

$\Delta_{EA1}H^{\ominus}$ is the enthalpy change when one mole of gaseous 1- ions are formed from a mole of gaseous atoms (by the capture of one electron per atom) at 298K and 101kPa.

This electron affinity will be EXOTHERMIC as the electron is attracted into the outer shell by the nucleus.
e.g. $Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}$ $\Delta_{EA1}H^{\ominus} = -346\ \text{kJ mol}^{-1}$

As with ionisation energies, we may need to use further electron affinities to form ions with 2- or higher charges, e.g.

$\Delta_{EA2}H^{\ominus}$ is the enthalpy change when an electron is added to each ion in a mole of gaseous 1- charged ions to produce gaseous 2- ions at 298K, 101kPa

This electron affinity, and subsequent additions of an electron will be ENDOTHERMIC because the incoming electron will be repelled by the negatively charged ion.

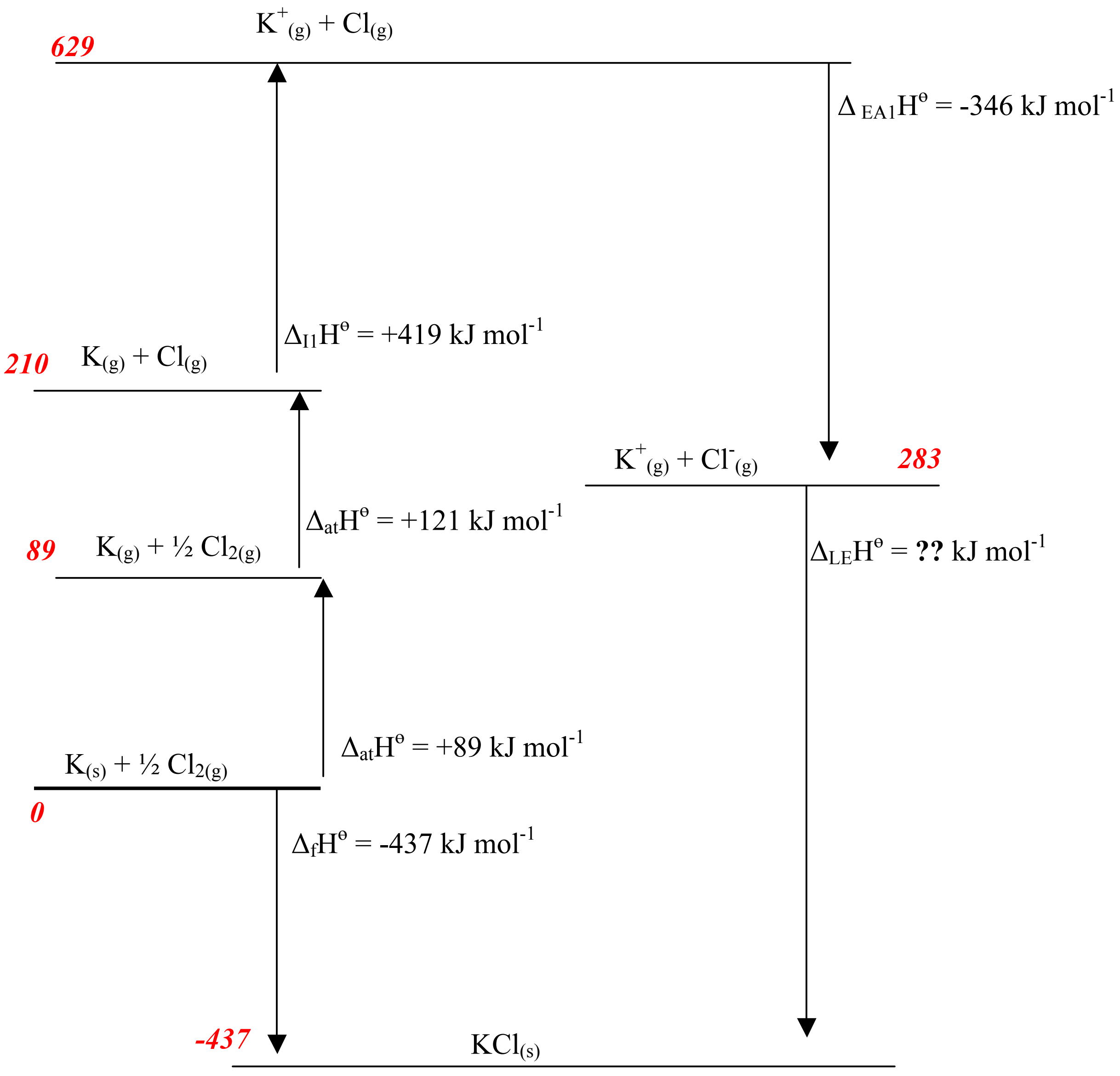
Constructing the Born-Haber cycle

Start with an energy level representing the elements in their standard states. This is the 'zero' energy point (or datum line) in the diagram. *Make this approximately ¼ of the way up from the bottom of the diagram.*

Now turn the elements into gaseous ions, and into the ionic lattice, step by step.

- endothermic steps take you to levels higher up the page
- exothermic steps take you to levels lower down
- label each level
- label each arrow with the appropriate ΔH, and the value if known

Worked example: a Born-Haber cycle for potassium chloride



The value of the enthalpy of lattice formation can now be found. There are several methods which can be used – one effective method is to now label each energy level on the diagram with its actual energy value, starting from the datum line with energy = 0, and using the known values to work out each level.

The direction of the arrow gives you a reminder as to what the sign of the energy change should be. Up = +ve, Down = -ve.

In our example, the lattice enthalpy arrow goes from +283 to -437 $kJmol^{-1}$ so the value of $\Delta H_{LE}^{\ominus} = -437 - 283 = -720$ $kJ\ mol^{-1}$

Note 1: You are not always working with one mole. Some Born-Haber cycles will require multiples of the relevant energy change, e.g. if forming $CaCl_2$, then you'll need $2\times\Delta_{EA}H$ to turn two $2Cl_{(g)}$ into $2Cl^-_{(g)}$ in order to form $CaCl_2$. You'll also need $2 \times \Delta_{at}H$ for the $Cl_{2(g)}$ to be turned into $2Cl_{(g)}$.

Note 2: Born-Haber cycles where the charge on the negative ion is more negative than -1 will go up in several steps, then down with the first $\Delta_{EA}H$ but then back up again with subsequent $\Delta_{EA}H$ values before the downwards lattice enthalpy step.

Practice:

Create Born-Haber cycles for the ionic compounds formed by:

- *A group 1 element with a group 7 element*
- *A group 1 element with a group 6 element*
- *A group 2 element with a group 7 element*
- *A group 2 element with a group 6 element*

Interpreting enthalpies of lattice formation

The more exothermic the value for lattice enthalpy of formation

- the larger the electrostatic forces of attraction
- the stronger ionic bonds
- the higher the melting point

There are two factors which govern the size of the lattice enthalpy:

- ionic size
- ionic charge

We can combine these two factors and consider **charge density**, the amount of charge divided by the size of the ion - the smaller an ion is, or the more highly charged it is, the greater its charge density.

As the ionic radius increases:

- the attraction between the ions decreases
- the lattice enthalpy becomes less exothermic (smaller value)

Therefore the compounds with the most exothermic lattice enthalpies will be those that have small, highly charged ions.

Explain the trend in lattice enthalpies for the sodium halides

$NaCl$ $\Delta_{LE}H = -787\ kJmol^{-1}$
$NaBr$ $= -751\ kJmol^{-1}$
NaI $= -705\ kJmol^{-1}$

The chloride ion is smaller than the bromide or iodide ion, and since they all have the same -1 charge, chloride ions have the largest charge density. This means they attract the Na^+ ions most strongly, leading to the most exothermic lattice enthalpy of the three compounds.

Describe, using ideas about lattice enthalpy, how the melting point of magnesium oxide is likely to differ from that of barium oxide.

The Mg^{2+} ions are smaller than the Ba^{2+} ions, and have the same charge. This means that Mg^{2+} ions have a higher charge density. There is a stronger attraction between the Mg^{2+} ions and the O^{2-} ions in MgO compared to the attraction between Ba^{2+} and O^{2-} in BaO. As a result the lattice enthalpy of MgO is more exothermic, and the lattice in MgO is stronger, resulting in a higher melting point for MgO than BaO.

Enthalpy change of solution and Enthalpy change of Hydration

When ionic compounds dissolve in water, there is usually a temperature change. Sometimes this is exothermic (e.g. dissolving calcium chloride) and sometimes endothermic (e.g. dissolving ammonium nitrate).

The experiments are easy to carry out in a laboratory, and the usual equations can be used to convert temperature change to enthalpy change. We can use the enthalpy change on dissolving an ionic lattice to construct a different **enthalpy cycle** to determine the lattice enthalpy, since this can't be measured directly. As before we will need some other enthalpy changes to construct the cycle.

The standard enthalpy change of solution

$\Delta_s H^{\ominus}$ Definition: The enthalpy change when one mole of an a substance dissolves in water under standard conditions of 298K and 101kPa

Equation: e.g. $KCl_{(s)} + aq \rightarrow K^+_{(aq)} + Cl^-_{(aq)}$ $\Delta_s H^{\ominus} = +26\ kJmol^{-1}$

When we measure enthalpy changes of solution directly, we find from the corresponding temperature changes that this can be either endothermic or exothermic. This is because solution involves the balance between two energy processes:

1) The breakdown of the lattice into GASEOUS ions (i.e. completely independent)
   - this requires energy, it is an endothermic step

2) The hydration of the ions, in which bonds are formed with water molecules
- this releases energy, an exothermic step

Breakdown of the ions

We want to turn solid lattice into gaseous ions – e.g. $KCl_{(s)} \rightarrow K^+_{(g)} + Cl^-_{(g)}$

This is just the OPPOSITE of the enthalpy of lattice formation, so we call it the **enthalpy of lattice dissociation**. The enthalpy change will have the same value as the lattice, but the opposite, positive (endothermic) sign.

e.g. Since $\Delta_{LE}H^\ominus$ for $CaCl_2$ = -2258 kJmol^{-1} then the enthalpy of lattice dissociation of $CaCl_2$ = +2258kJmol^{-1}

Hydration of the ions

The gaseous ions surround themselves by strongly attracting water molecules. It's actually a kind of bonding that you'll explore further when discussing complexes. Positively charged ions attract the δ- oxygen atom of water molecules, while negative ions attract the δ+ hydrogen atoms. When these bonds are formed, energy is released; this is the enthalpy of hydration of each ion.

<u>The standard enthalpy change of hydration</u>

$\Delta_{hyd}H^\ominus$ The enthalpy change when one mole of aqueous ions are formed from their gaseous ions under standard conditions of 298K and 101kPa

e.g. $K^+_{(g)} + aq \rightarrow K^+_{(aq)}$ $\Delta_{hyd}H^\ominus$ = -322 kJmol^{-1}

$Cl^-_{(g)} + aq \rightarrow Cl^-_{(aq)}$ $\Delta_{hyd}H^\ominus$ = -363 kJmol^{-1}

What affects the enthalpies of hydration ?

As with enthalpies of lattice formation, the factors that affect enthalpies of hydration are ionic charge and ionic radius - which we can combine as **charge density**

The larger the charge density of an ion, the more strongly it attracts water molecules, and the more exothermic the enthalpy change of hydration will be.

For ions of the same charge, as the <u>ionic radius</u> becomes smaller, the charge density increases, and $\Delta_{hyd}H^\ominus$ becomes more exothermic.

e.g.	Cl^-	enthalpy of hydration -363 kJmol^{-1}	
	Br^-	-336	↓ inc. size
	I^-	-295	

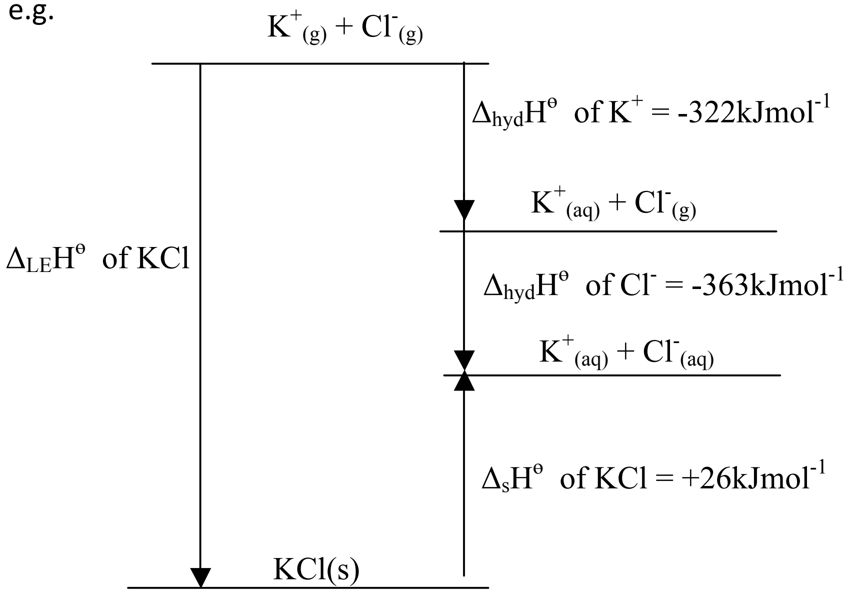
As the charge on the ion increases, the charge density increases, and the hydration enthalpy becomes more exothermic. Note that when comparing ions in the same period, as we go across the period the ions get smaller as well as more highly charged:

e.g.	Na^+	-406	↓ size decreases AND charge increases
	Mg^{2+}	-1921	
	Al^{3+}	- 4665	

Combining these in an Enthalpy Cycle

We can measure an enthalpy of solution, and use published enthalpies of hydration, combining these into an enthalpy cycle to determine the lattice enthalpy.

e.g.



Any 'missing' value can be worked out knowing the other enthalpy changes.

Here, if we use the values of $\Delta_{hyd}H^\ominus$ and $\Delta_sH^\ominus$ then we find that:

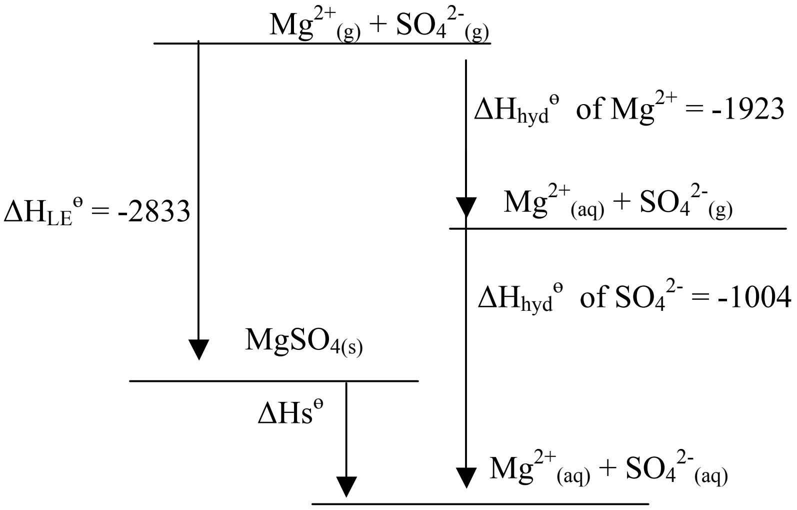
$$\Delta_{LE}H^\ominus = -322 + (-363) - 26 \qquad = -711 \text{ kJmol}^{-1}$$

Note:

- Any compound which contains more than one of an ion, e.g. $MgCl_2$, will require a multiple of the enthalpy of hydration of chloride ions in the cycle, x2 in this case.
- The enthalpy of solution can also be exothermic, so the arrow from the energy level of the solid lattice would go downward for $\Delta_sH^\ominus$

Work out the enthalpies of solution of magnesium sulphate and barium sulphate, given the following data:

Enthalpy of lattice formation of $MgSO_4$ = -2833 $kJmol^{-1}$
Enthalpy of lattice formation of $BaSO_4$ = -2474 $kJmol^{-1}$
Enthalpy of hydration of Mg^{2+} = -1923 $kJmol^{-1}$
Enthalpy of hydration of Ba^{2+} = -1364 $kJmol^{-1}$
Enthalpy of hydration of SO_4^{2-} = -1004 $kJmol^{-1}$



For $MgSO_4$ Δ_sH = -1923 + (-1004) – (-2833) = -94 $kJmol^{-1}$
For $BaSO_4$, Δ_sH = -1364 + (-1004) – (-2474) = +106 $kJmol^{-1}$

Interpreting the values of enthalpies of solution

Magnesium sulphate is quite soluble in water, while barium sulphate is virtually insoluble. The enthalpy change of solution for magnesium sulphate is exothermic, while the enthalpy change of solution for barium sulphate is endothermic.

Could we predict whether enthalpy of solutions are exothermic or endothermic ?
No - it depends whether the energy needed to break the lattice is more or less than the energy released when the ions are hydrated. There are two competing factors, both of which are dependent on charge density, and we don't know which will have the more significant effect.

Can we predict solubility?
We can't predict solubility purely on the basis of comparing the sizes and charges of the ions, but we can form an enthalpy cycle to determine how exothermic or endothermic the enthalpy of solution is.

Enthalpies of solution are good for comparing the solubilities of compounds, rather than predicting the solubility of an individual substance. This is because enthalpy changes are NOT the only factor that affects the solubility – **entropy** (in a different topic) also has an effect.

Practice Qs:

1. Use the data to calculate the enthalpies of solution of silver iodide and silver chloride.

Enthalpy of hydration of Ag^+	-464.4 $kJmol^{-1}$
Enthalpy of hydration of Cl^-	-384.1
Enthalpy of hydration of I^-	-306.7
Lattice enthalpy of AgCl	-890.0
Lattice enthalpy of AgI	-867.0

2. Name these three enthalpy changes

$Na^+_{(g)} + F^-_{(g)} \rightarrow NaF_{(s)}$	ΔH =	-918 $kJmol^{-1}$
$Na^+_{(g)} + aq \rightarrow Na^+_{(aq)}$		-390 $kJmol^{-1}$
$NaF_{(s)} + aq \rightarrow Na^+_{(aq)} + F^-_{(aq)}$		+71 $kJmol^{-1}$

Write an equation, including state symbols, for the enthalpy change of hydration of F^- ions.

Use the data to calculate the enthalpy change of hydration of F^- ions.

Answers:

1: ΔH_s AgCl = 890 – (464.4 + 384.1) = + 41.5 $kJmol^{-1}$

ΔH_s AgI = 867 – (464.4 + 306.7) = + 95.9 $kJmol^{-1}$

We know both are insoluble – tests for halide ions in solution…

2:
- lattice enthalpy of sodium fluoride
- enthalpy of hydration of sodium
- enthalpy of solution of sodium fluoride

$F^-_{(g)} + aq \rightarrow F^-_{(aq)}$

ΔH_{hyd} F^- = -918 + (390 + 71) = -457 $kJmol^{-1}$