A2
LEVEL

CHEMISTRY
FOR CCEA A2 LEVEL

COLOURPOINT
EDUCATIONAL

Dr Wingfield Glassey

The Author

Dr Wingfield Glassey teaches Chemistry at Friends' School Lisburn, and is an examiner for GCE AS and A2 Chemistry. Dr Glassey also maintains a professional interest in the teaching and learning of science, and has published scholarly articles in a number of peer-reviewed journals including *The Journal of Chemical Education*. He maintains a web site containing resources for A-Level Chemistry at http://wglassey.me.uk

Copyright

Publisher's Note: This book has been through a rigorous quality assurance process by an independent person experienced in the CCEA specification prior to publication. It has been written to help students preparing for the A2 Chemistry specification from CCEA. While Colourpoint Educational, the author and the quality assurance person have taken every care in its production, we are not able to guarantee that the book is completely error-free. Additionally, while the book has been written to closely match the CCEA specification, it is the responsibility of each candidate to satisfy themselves that they have fully met the requirements of the CCEA specification prior to sitting an exam set by that body. For this reason, and because specifications change with time, we strongly advise every candidate to avail of a qualified teacher and to check the contents of the most recent specification for themselves prior to the exam. Colourpoint Creative Ltd therefore cannot be held responsible for any errors or omissions in this book or any consequences thereof.

CONTENTS

Unit A2 1: Further Physical and Organic Chemistry

Unit A2 2: Analytical, Transition Metals, Electrochemistry and Organic Nitrogen Chemistry

Unit A2 3: Further Practical Chemistry

Unit A2 1:

Further Physical and Organic Chemistry

4.1 Energetics: Solids and Solutions

Previously, at AS Level, we used Hess's Law to determine enthalpy changes that could not be measured in the laboratory. In this section we examine how Hess's Law can be used to determine enthalpy changes for reactions involving solids and solutions.
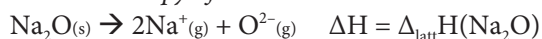
Lattice Enthalpy

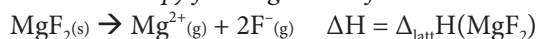**In this section we are learning to:**

- Explain what is meant by the lattice enthalpy of an ionic compound.
- Account for trends in the lattice enthalpies of ionic compounds.

An ionic compound is made up of cations and anions packed tightly in an ordered lattice. The ionic lattice in solid sodium chloride is illustrated in Figure 1. The compound is held together by strong attractive forces between oppositely charged ions in the lattice. The strength of the ionic bonding between the ions in the lattice is measured by the lattice enthalpy of the compound. The **lattice enthalpy** of an ionic compound, $\Delta_{latt}H$ is *the enthalpy change when one mole of an ionic compound is converted to gas phase ions.*

Lattice enthalpy of sodium oxide:
$$Na_2O_{(s)} \rightarrow 2Na^+_{(g)} + O^{2-}_{(g)} \quad \Delta H = \Delta_{latt}H(Na_2O)$$

Lattice enthalpy for magnesium fluoride:
$$MgF_{2(s)} \rightarrow Mg^{2+}_{(g)} + 2F^-_{(g)} \quad \Delta H = \Delta_{latt}H(MgF_2)$$

The lattice enthalpies for Group I and Group II fluorides in Figure 2a demonstrate that lattice enthalpy decreases as the metal ions get bigger and the distance between neighbouring ions increases down the group. The comparison also demonstrates that the lattice enthalpies of the Group II fluorides are significantly greater than the corresponding Group I fluorides. This results from greater attraction between neighbouring ions as the charge on the metal ions increases.
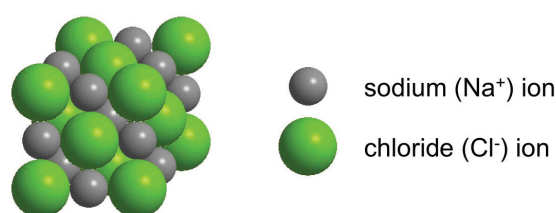
Figure 1: The ionic lattice in sodium chloride, NaCl. The sodium cations are surrounded by chloride anions and vice versa.

Similarly, Figure 2b demonstrates that the lattice enthalpy of a Group II oxide is greater than that of the corresponding Group II fluoride as the charge on an oxide (O^{2-}) ion is greater than the charge on a fluoride (F^-) ion in the corresponding Group II fluoride. The effect of ion size and charge on the lattice enthalpy of an ionic compound is summarised in Figure 3.

Exercise 4.1A

1. The strength of the ionic bonding in compounds, such as magnesium fluoride and magnesium chloride, is related to the lattice enthalpy of the compound. Define the term *lattice enthalpy*.

    (CCEA January 2011)

2. Which one of the following equations represents the lattice enthalpy of sodium chloride?

    A $NaCl_{(aq)} \rightarrow Na_{(g)} + Cl_{(g)}$
    B $NaCl_{(aq)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$
    C $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$
    D $NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$

    (CCEA May 2012)

(a)

(b)
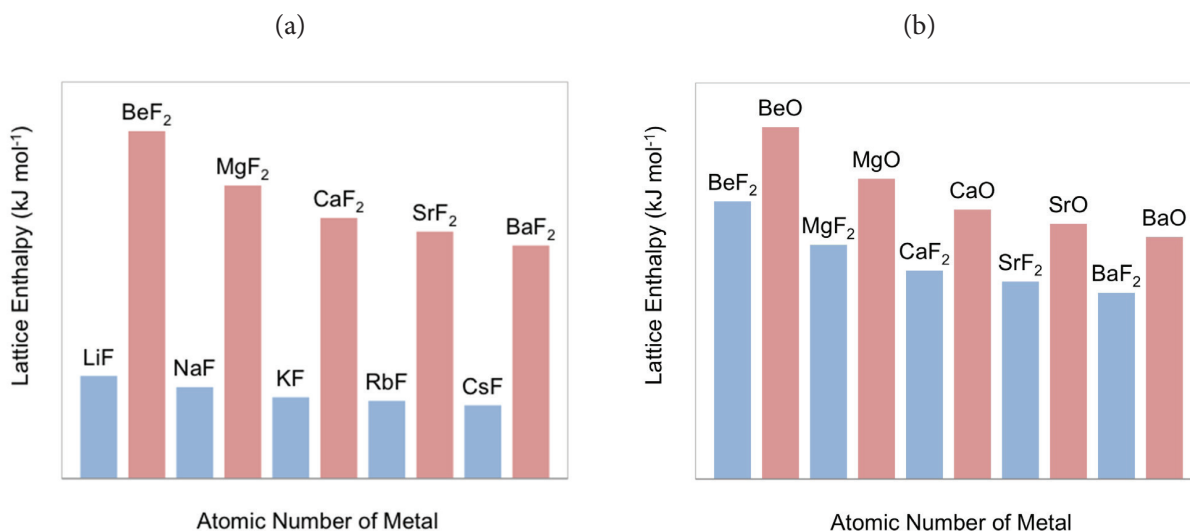
Figure 2: Comparison of the lattice enthalpy for (a) Group I and Group II fluorides, and (b) Group II oxides and fluorides.
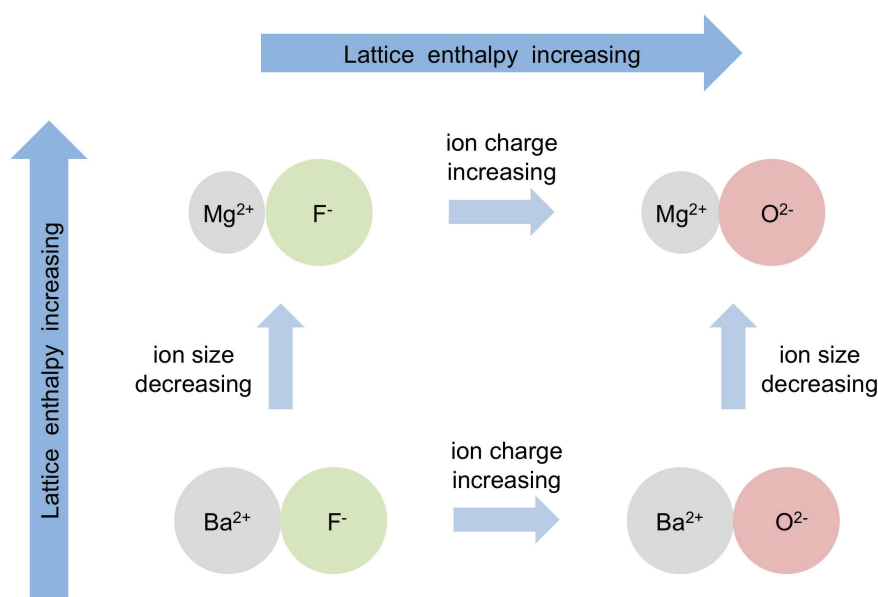
Figure 3: The effect of ion size and charge on the magnitude of the lattice enthalpy for an ionic compound.

3. Which one of the following equations represents the lattice enthalpy of calcium bromide?

A $\quad Ca_{(s)} + Br_{2(l)} \rightarrow CaBr_{2(s)}$

B $\quad CaBr_{2(s)} \rightarrow Ca_{(s)} + Br_{2(g)}$

C $\quad Ca^{2+}_{(g)} + 2Br^-_{(g)} \rightarrow CaBr_{2(g)}$

D $\quad CaBr_{2(s)} \rightarrow Ca^{2+}_{(g)} + 2Br^-_{(g)}$

(CCEA May 2009)

4. Values for the lattice enthalpies of the calcium halides are given in the following table. (a) Explain why all of these values are positive.

(b) Suggest why the values of the lattice enthalpies for the calcium halides decrease as Group VII is descended.

CaF$_2$	CaCl$_2$	CaBr$_2$	CaI$_2$
+2630	+2258	+2176	+2074

(CCEA May 2015)

5. The lattice enthalpies for Group I chlorides are listed in the following table. Suggest why the lattice enthalpy decreases as you descend the group.

Salt	Lattice enthalpy, kJ mol^{-1}
Lithium chloride	848
Sodium chloride	780
Potassium chloride	711
Rubidium chloride	685
Caesium chloride	661

(CCEA January 2010)

6. Suggest why the lattice enthalpies of the magnesium halides in the following table decrease.

	Lattice enthalpy, kJ mol^{-1}
Magnesium fluoride	+2913
Magnesium bromide	+2097
Magnesium iodide	+1944

(Adapted from CCEA January 2009)

7. (a) Write the equation for the lattice enthalpy of magnesium chloride. (b) Explain why the lattice enthalpy for sodium chloride is less than the lattice enthalpy for magnesium chloride.

(CCEA June 2005)

Before moving to the next section, check that you are able to:

- Define the *lattice enthalpy* of an ionic compound.
- Account for trends in the lattice enthalpies of ionic compounds in terms of the size and charge of the ions in the compounds.

Born-Haber Cycles

In this section we are learning to:

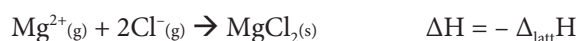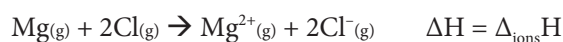- Construct a Born-Haber cycle for an ionic compound.

The lattice enthalpy of an ionic compound cannot be measured directly and must instead be calculated from enthalpy changes that can be measured. This is accomplished by using Hess's Law to construct a type of enthalpy diagram known as a **Born-Haber cycle**. The Born-Haber cycle for an ionic compound relates the enthalpy changes associated with forming the compound from its elements.

The **standard enthalpy of formation**, $\Delta_f H^\circ$ of a compound is *the enthalpy change when one mole of the compound is formed from its elements under standard conditions.*

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)} \qquad \Delta H = \Delta_f H^\circ$$
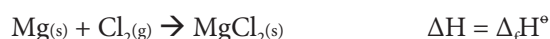
This is equivalent to first converting atoms of each element into gas phase atoms ($\Delta_{atoms}H$), and then into gas phase ions ($\Delta_{ions}H$), before finally using the gas phase ions to form the compound ($-\Delta_{latt}H$).

$$Mg_{(s)} + Cl_{2(g)} \rightarrow Mg_{(g)} + 2Cl_{(g)} \qquad \Delta H = \Delta_{atoms}H$$

$$Mg_{(g)} + 2Cl_{(g)} \rightarrow Mg^{2+}{}_{(g)} + 2Cl^-{}_{(g)} \qquad \Delta H = \Delta_{ions}H$$

$$Mg^{2+}{}_{(g)} + 2Cl^-{}_{(g)} \rightarrow MgCl_{2(s)} \qquad \Delta H = -\Delta_{latt}H$$

> *Applying Hess's law gives:*
> $\Delta_f H^\circ = \Delta_{atoms}H + \Delta_{ions}H - \Delta_{latt}H$ Equation 1

This relationship can be represented in the form of a Born-Haber cycle. The Born-Haber cycle for $MgCl_2$ in given in Figure 4 and is similar to the Born-Haber cycles for other ionic compounds. The lattice enthalpy, $\Delta_{latt}H$ is endothermic as energy is needed to overcome the attractive forces between oppositely charged ions in the lattice. The enthalpy change $\Delta_{atoms}H$ is also endothermic as energy is required to break the bonds between the atoms in the elements. For most ionic compounds, the enthalpy change $\Delta_{ions}H$ is also endothermic as the energy needed to ionise the metal atoms is greater than the energy released on adding electrons to the non-metal atoms. In contrast, the standard enthalpy of formation, $\Delta_f H^\circ$ for an ionic compound is exothermic as the energy released when the ions bond to form the lattice is greater than the energy needed to break bonds in the elements.
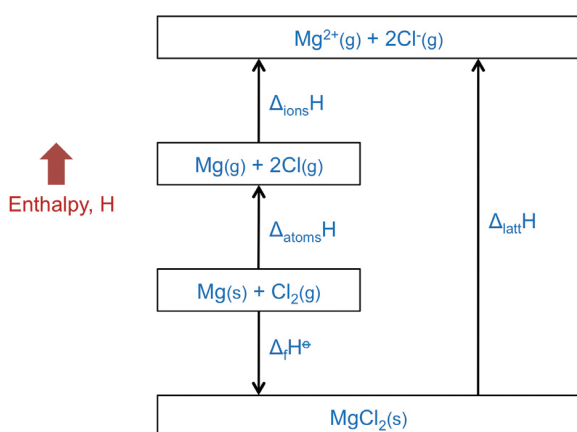
Figure 4: A Born-Haber cycle for magnesium chloride, MgCl₂.

Forming Atoms from Elements

In the case of $MgCl_2$, $\Delta_{atoms}H$ is the enthalpy change when one mole of gas phase magnesium atoms and two moles of gas phase chlorine atoms are formed from magnesium and chlorine in their standard states: $Mg_{(s)}$ and $Cl_{2(g)}$.
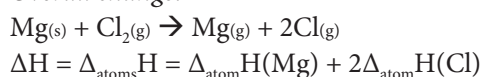
Forming magnesium atoms:
$Mg_{(s)} \rightarrow Mg_{(g)}$ $\Delta H = \Delta_{atom}H(Mg)$

Forming chlorine atoms:
$Cl_{2(g)} \rightarrow 2Cl_{(g)}$ $\Delta H = 2\Delta_{atom}H(Cl)$

Overall change:
$Mg_{(s)} + Cl_{2(g)} \rightarrow Mg_{(g)} + 2Cl_{(g)}$
$\Delta H = \Delta_{atoms}H = \Delta_{atom}H(Mg) + 2\Delta_{atom}H(Cl)$

The **enthalpy of atomisation**, $\Delta_{atom}H$ of an element is *the enthalpy change when one mole of gas phase atoms are formed from the element in its standard state.*
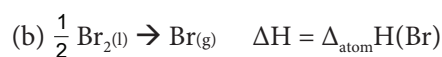
Worked Example 4.1i

Write the equation used to define the enthalpy of atomisation for (a) iron, (b) bromine and (c) phosphorus.

Strategy

- Recall that atomisation is the process of turning atoms in their standard state into atoms in the gas phase.
- Recall that under standard conditions: iron is a

metal, bromine is a diatomic liquid and phosphorus is a molecular solid with formula P_4.

Solution

(a) $Fe_{(s)} \rightarrow Fe_{(g)}$ $\Delta H = \Delta_{atom}H(Fe)$

(b) $\frac{1}{2} Br_{2(l)} \rightarrow Br_{(g)}$ $\Delta H = \Delta_{atom}H(Br)$

(c) $\frac{1}{4} P_{4(s)} \rightarrow P_{(g)}$ $\Delta H = \Delta_{atom}H(P)$

Before moving to the next section, check that you are able to:

- Define the *standard enthalpy of formation* of an ionic compound.
- Define the *enthalpy of atomisation* of an element.
- Explain how Hess's Law can be used to relate the enthalpy of formation and lattice enthalpy of an ionic compound by constructing a Born-Haber cycle.

Forming Ions from Atoms

In the case of $MgCl_2$, $\Delta_{ions}H$ corresponds to the enthalpy change when one mole of gas phase magnesium atoms are converted to Mg^{2+} ions, and two moles of gas phase chlorine atoms are converted to Cl^- ions.
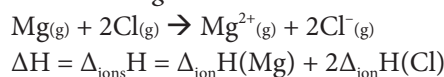
Forming magnesium ions:
$Mg_{(g)} \rightarrow Mg^{2+}_{(g)}$ $\Delta H = \Delta_{ion}H(Mg)$

Forming chloride ions:
$2Cl_{(g)} \rightarrow 2Cl^-_{(g)}$ $\Delta H = 2\Delta_{ion}H(Cl)$

Overall change:
$Mg_{(g)} + 2Cl_{(g)} \rightarrow Mg^{2+}_{(g)} + 2Cl^-_{(g)}$
$\Delta H = \Delta_{ions}H = \Delta_{ion}H(Mg) + 2\Delta_{ion}H(Cl)$

The enthalpy change to form Mg^{2+} ions from gas phase magnesium atoms, $\Delta_{ion}H(Mg)$ is the sum of the first and second ionisation energies (IE1 and IE2) for magnesium.

$Mg_{(g)} \rightarrow Mg^+_{(g)} + e^-$ $\Delta H = IE1(Mg)$

$Mg^+_{(g)} \rightarrow Mg^{2+}_{(g)} + e^-$ $\Delta H = IE2(Mg)$

$Mg_{(g)} \rightarrow Mg^{2+}_{(g)} + 2e^-$ $\Delta H = \Delta_{ion}H(Mg)$
                                $= IE1(Mg) + IE2(Mg)$
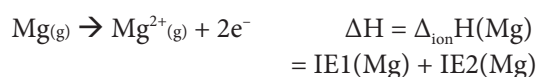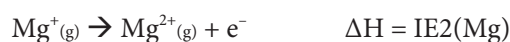
The enthalpy change to form Cl^- ions from gas phase chlorine atoms, $\Delta_{ion}H(Cl)$ is the first electron affinity for chlorine, $EA1(Cl)$.

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad \Delta H = \Delta_{ion}H(Cl) = EA1(Cl)$$
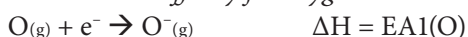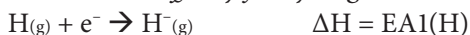
The **first electron affinity** (EA1) of an element is *the enthalpy change when one mole of electrons is added to one mole of gas phase atoms to form gas phase ions with a charge of 1–.*

First electron affinity for oxygen:
$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad \Delta H = EA1(O)$

First electron affinity for hydrogen:
$H_{(g)} + e^- \rightarrow H^-_{(g)} \qquad \Delta H = EA1(H)$

The first electron affinity, EA1 for oxygen, fluorine and other electronegative elements is very exothermic. Less electronegative elements have a smaller EA1.

The **second electron affinity** (EA2) of an element is *the enthalpy change when one mole of electrons is added to one mole of gas phase ions with a charge of 1– to form gas phase ions with a charge of 2–.*

Second electron affinity for chlorine:
$Cl^-_{(g)} + e^- \rightarrow Cl^{2-}_{(g)} \qquad \Delta H = EA2(Cl)$

Second electron affinity for oxygen:
$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad \Delta H = EA2(O)$
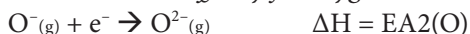
The second electron affinity, EA2 is endothermic as energy is required to overcome the repulsion when an electron is added to a negatively charged ion.

Exercise 4.1B

1. Which one of the following reactions in the Born-Haber cycle for potassium iodide is exothermic?

   A $KI_{(s)} \rightarrow K^+_{(g)} + I^-_{(g)}$

   B $K_{(g)} \rightarrow K^+_{(g)} + e^-$

   C $I_{2(g)} \rightarrow 2I_{(g)}$

   D $I_{(g)} + e^- \rightarrow I^-_{(g)}$

   (CCEA May 2008)

2. Which one of the following has a positive enthalpy value?

   A $Na_{(g)} \rightarrow Na_{(s)}$

   B $Na^+_{(g)} + e^- \rightarrow Na_{(g)}$

   C $O_{(g)} + e^- \rightarrow O^-_{(g)}$

   D $O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)}$

   (CCEA June 2014)

3. The energy produced when an electron is added to an isolated atom would be the highest for elements in:

   A Group I

   B Group III

   C Group VII

   D Group VIII

   (CCEA January 2012)

4. The lattice enthalpies for potassium chloride and potassium bromide are $+710$ kJ mol^{-1} and $+679$ kJ mol^{-1} respectively. (a) State three other enthalpy changes that would differ in the Born-Haber cycles for these compounds. (b) Explain why these enthalpy changes differ for each compound.

   (CCEA May 2013)

5. For which one of the following chlorides is it not possible to construct a Born-Haber cycle?

   A AgCl   B HCl

   C RbCl   D $MgCl_2$

   (CCEA January 2007)

Before moving to the next section, check that you are able to:

- Explain the changes that occur when gaseous atoms are converted to gaseous ions.
- Define the *first and second ionisation energies* of an element.
- Define the *first and second electron affinities* of an element.
- Recall the relationship between the electronegativity of an element and the size of EA1.
- Explain why EA2 is endothermic.

Working with Born-Haber Cycles

In this section we are learning to:

- Use a Born-Haber cycle to calculate enthalpy changes associated with the formation of an ionic compound.

Calculating Lattice Enthalpy

While all Born-Haber cycles have the same basic form as the cycle for $MgCl_2$ in Figure 4, the individual enthalpy changes that make up $\Delta_{atoms}H$ and $\Delta_{ions}H$ may be organised or grouped differently, making the cycle appear more complex.

Often, the goal of constructing a Born-Haber cycle is to calculate the lattice enthalpy, $\Delta_{latt}H$ for an ionic compound. The relationship between Δ_fH°, $\Delta_{atoms}H$, $\Delta_{ions}H$ and $\Delta_{latt}H$ obtained by applying Hess's Law (Equation 1, page 7) can be rearranged to give an equation that can be used to calculate the lattice enthalpy (Equation 2, below).
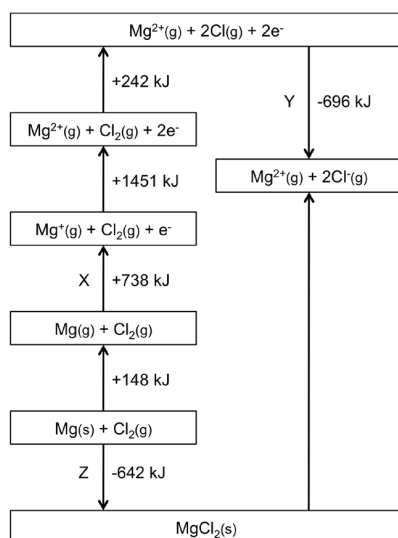
Equation to calculate lattice enthalpy:
$$\Delta_{latt}H = \Delta_{atoms}H + \Delta_{ions}H - \Delta_fH^\circ \qquad \text{Equation 2}$$

Worked Example 4.1ii

Magnesium chloride is an ionic compound. The Born-Haber cycle for the formation of magnesium chloride is shown in the following diagram.

(a) Name the energy changes X, Y and Z.

(b) Calculate the lattice enthalpy for magnesium chloride

(CCEA May 2010)

Strategy
- Use the definitions of $\Delta_{atom}H$, IE1, IE2 and EA1 to identify X, Y and Z.
- Combine the individual enthalpy changes to calculate $\Delta_{atoms}H$ and $\Delta_{ions}H$.
- Use the relationship between $\Delta_{latt}H$, $\Delta_{atoms}H$, $\Delta_{ions}H$ and Δ_fH° (Equation 2) to calculate the lattice enthalpy.

Solution

(a) X represents the first ionisation energy for magnesium.

Y represents twice the electron affinity of chlorine.

Z represents the enthalpy of formation of magnesium chloride.

(b) $\Delta_{atoms}H = \Delta_{atom}H(Mg) + 2\,\Delta_{atom}H(Cl)$
$= 148 + 242 = 390 \text{ kJ mol}^{-1}$

$\Delta_{ions}H = IE1(Mg) + IE2(Mg) + 2\,EA1(Cl)$
$= 738 + 1451 + (-696) = 1493 \text{ kJ mol}^{-1}$

$\Delta_{latt}H = \Delta_{atoms}H + \Delta_{ions}H - \Delta_fH^\circ$
$= 390 + 1493 - (-642) = 2525 \text{ kJ mol}^{-1}$

Exercise 4.1C

1 (a) Complete the Born-Haber cycle for magnesium fluoride shown in the following diagram.

(b) Use the data in the table to calculate the lattice enthalpy for magnesium fluoride.
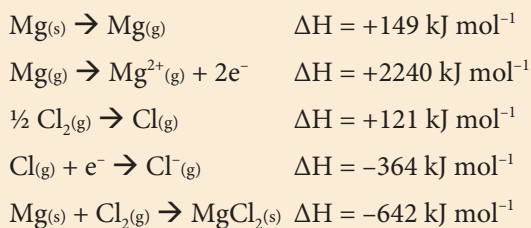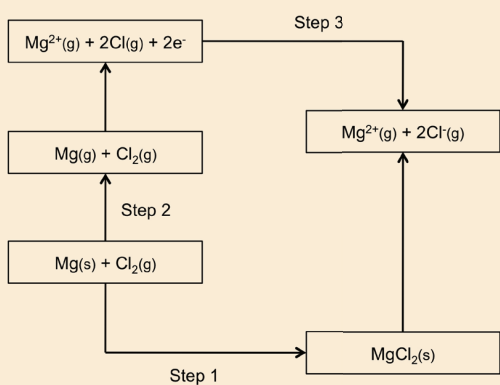
	kJ mol^{-1}
Standard enthalpy of formation for magnesium fluoride	−1123
First electron affinity of fluorine	−348
Atomisation enthalpy of fluorine	79
First ionisation enthalpy of magnesium	736
Second ionisation enthalpy of magnesium	1450
Atomisation enthalpy of magnesium	150
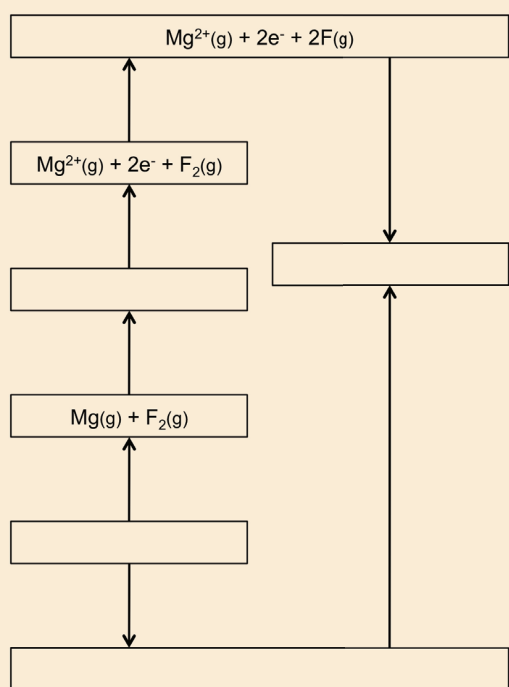
(CCEA January 2011)

2. The lattice enthalpy of magnesium chloride can be calculated using the following diagram.

(a) What name is given to this type of diagram?
(b) Identify the type of energy change that occurs in Steps 1, 2 and 3. (c) Use the information given below to calculate the lattice enthalpy of magnesium chloride.


$Mg_{(s)} \rightarrow Mg_{(g)}$ $\Delta H = +149$ kJ mol^{-1}

$Mg_{(g)} \rightarrow Mg^{2+}_{(g)} + 2e^-$ $\Delta H = +2240$ kJ mol^{-1}

$\frac{1}{2} Cl_{2(g)} \rightarrow Cl_{(g)}$ $\Delta H = +121$ kJ mol^{-1}

$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ $\Delta H = -364$ kJ mol^{-1}

$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$ $\Delta H = -642$ kJ mol^{-1}

(CCEA January 2014)

3. A Born-Haber cycle for potassium iodide is shown in the following diagram. The lattice enthalpy is labelled. Other enthalpy changes are shown by the letters A to E. (a) State which letter (A to E) represents:
(i) the standard enthalpy of formation of potassium iodide.
(ii) the first electron affinity of iodine.
(iii) the first ionisation energy of potassium.
(iv) the enthalpy of atomisation of potassium.

(b) Use the data in the table to calculate the lattice enthalpy of potassium iodide.

| Enthalpy change	A	B	C	D	E
ΔH / kJ mol^{-1}	89.5	420.0	106.6	−295.4	−327.6
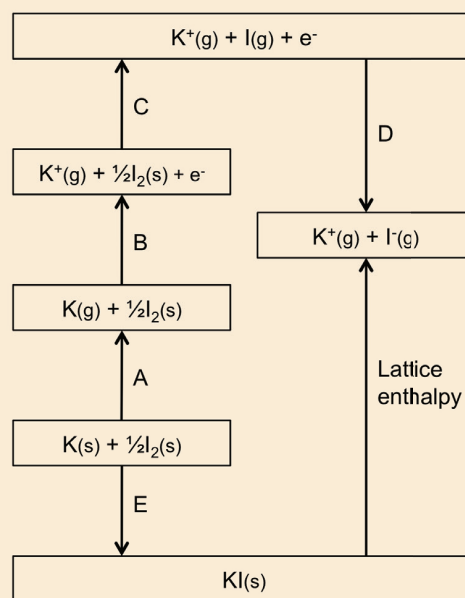
(CCEA May 2013)

Calculating Other Enthalpy Changes

The relationship between $\Delta_{latt}H$, $\Delta_{atoms}H$, $\Delta_{ions}H$ and $\Delta_f H^{\ominus}$ in Equation 2 can also be used to calculate one of the contributions to $\Delta_{atoms}H$ or $\Delta_{ions}H$ such as IE1 or EA1.
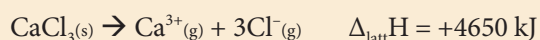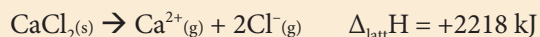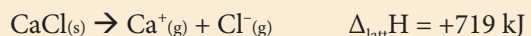
Exercise 4.1D

1. (a) Complete the Born-Haber cycle for the formation of magnesium chloride in the following diagram. (b) Use the data in the table to calculate the electron affinity of chlorine.

	kJ mol^{-1}
Standard enthalpy of formation for magnesium chloride	−642
Lattice enthalpy for magnesium chloride	2493
Atomisation enthalpy of chlorine	121
First ionisation enthalpy of magnesium	736
Second ionisation enthalpy of magnesium	1450
Atomisation enthalpy of magnesium	150

$Mg^{2+}(g) + 2Cl^-(g)$

$Mg(s) + Cl_2(g)$

$MgCl_2(s)$
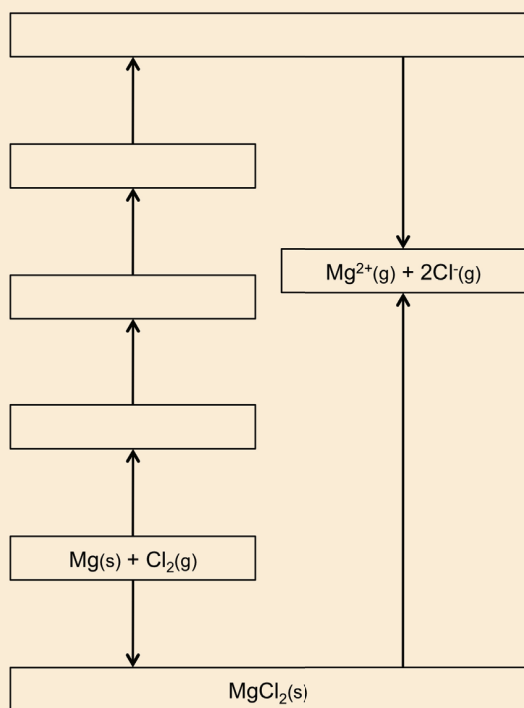
(CCEA May 2011)

2. Calcium could form the chlorides CaCl and CaCl$_3$. The following lattice enthalpies were calculated using the theoretical sizes of the ions.

$CaCl_{(s)} \rightarrow Ca^+(g) + Cl^-(g)$ $\quad \Delta_{latt}H = +719$ kJ

$CaCl_{2(s)} \rightarrow Ca^{2+}(g) + 2Cl^-(g)$ $\quad \Delta_{latt}H = +2218$ kJ

$CaCl_{3(s)} \rightarrow Ca^{3+}(g) + 3Cl^-(g)$ $\quad \Delta_{latt}H = +4650$ kJ

(a) Use the thermodynamic values in the following table, together with the appropriate lattice enthalpy, to calculate the enthalpy of formation for CaCl$_{3(s)}$. (b) Use the enthalpy of formation to explain why CaCl$_3$ does not exist. (c) Explain why the lattice enthalpies increase from CaCl to CaCl$_2$ to CaCl$_3$.

first ionisation energy of calcium	= +590 kJ mol^{-1}
second ionisation energy of calcium	= +1145 kJ mol^{-1}
third ionisation energy of calcium	= +4912 kJ mol^{-1}
standard enthalpy of atomisation of chlorine	= +112 kJ mol^{-1}
standard enthalpy of atomisation of calcium	= +178 kJ mol^{-1}
electron affinity of chlorine	= −349 kJ mol^{-1}

(CCEA May 2015)

Before moving to the next section, check that you are able to:

- Identify the individual enthalpy changes used to construct a Born-Haber cycle.
- Complete the Born-Haber cycle for an ionic compound.
- Use a Born-Haber cycle to calculate one of the enthalpy changes associated with the formation of an ionic compound.

Using Bond Enthalpy Values

In elements such as chlorine (Cl$_2$) and oxygen (O$_2$) the enthalpy of atomisation, $\Delta_{atom}H$ can be simply related to the bond enthalpy for the bonds in the element. *In this context the term bond enthalpy (E) refers to the energy needed to break one mole of bonds of a specified type in the element.*