Chem Factsheet

January 2002 Number 28

Energetics - Lattice Enthalpy and Born-Haber Cycle

To succeed with this topic you need to :

- **Ensure you understand the AS work on enthalpy cycles and Hess's Law (covered in Factsheet No. 8);**
- **Ensure you understand the terms ionisation energy and electron affinity (covered in Factsheet No. 1.).**

After working through this Factsheet you will:

- **have met the new enthalpy terms of Lattice Enthalpy and Standard Enthalpy of Atomisation;**
- **be able to write Born-Haber cycles for any ionic compound;**
- **be able to use these cycles for calculation work;**
- **understand the significance of variations in Lattice Enthalpy values and what this tells us about the ions in a compound;**
- **be able to explain trends in Lattice Enthalpy values.**

This Factsheet introduces the Born-Haber cycle, and Factsheet No. 29 ('How to Answer Questions on Born-Haber Cycles') goes into the details of examination questions and calculations.

***Exam Hint**: - Candidates should be aware that:*
- *There are 'easy marks' available for any candidate who learns and can write the definition for Lattice Enthalpy and standard enthalpy of atomisation;*
- *If a Born-Haber cycle calculation is worth 5 marks, 3 marks will be for writing the correct cycle;*
- *State symbols are important – if omitted from the cycle marks are deducted;*
- *The differences in LE values is invariably tested and, once understood by candidates, should give some 'easy marks'.*

Standard Enthalpy of Atomisation, $\triangle H^{\ominus}_{298.at}$

Standard enthalpy of Atomisation ($\triangle H^{\ominus}_{298.at}$) is the energy required to produce 1 mole of gaseous atoms of an element under standard conditions (298K, 1 atmosphere pressure).

$\triangle H^{\ominus}_{298.at}$ needs to be looked at carefully as these following examples show:

$\triangle H^{\ominus}_{298.at}$ [Na(s)] $\quad Na(s) \rightarrow Na(g)$

$\triangle H^{\ominus}_{298.at}$ [Mg(s)] $\quad Mg(s) \rightarrow Mg(g)$

$\triangle H^{\ominus}_{298.at}$ [$\frac{1}{2}Cl_2(g)$] $\quad \frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

$\triangle H^{\ominus}_{298.at}$ [$\frac{1}{2}O_2(g)$] $\quad \frac{1}{2}O_2(g) \rightarrow O(g)$

You need to see the differences between solids converting to gases, and diatomic gaseous elements converting to gaseous atoms. These equations are all based on producing **1 mole of gaseous atoms**.

For practice on writing $\triangle H^{\ominus}_{298.at}$ equations go to question 1.

Lattice Enthalpy (LE)

Lattice Enthalpy (LE) is the energy produced when 1 mole of a solid ionic compound is made from its gaseous ions under standard conditions (298K, 1 atmosphere pressure).

i.e. $M^+(g) + X^-(g) \rightarrow MX(s) \quad \triangle H = LE$ *is the general equation for LE.*

These are further specific examples:

$Na^+(g)$	+	$Cl^-(g)$	$\rightarrow$	$NaCl(s)$
$Mg^{2+}(g)$	+	$O^{2-}(g)$	$\rightarrow$	$MgO(s)$
$2K^+(g)$	+	$O^{2-}(g)$	$\rightarrow$	$K_2O(s)$
$Ca^{2+}(g)$	+	$2Cl^-(g)$	$\rightarrow$	$CaCl_2(s)$

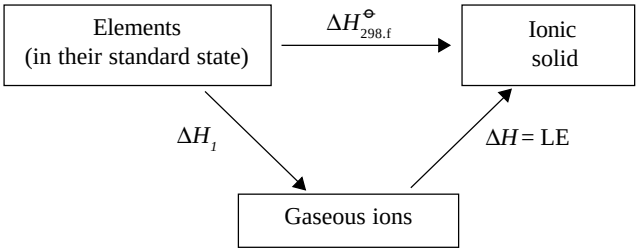
For practice on writing L.E. equations go to question 2.

***Remember** : - all L.E. values are **negative** and given in kJ mol^{-1}*
- *This unit is the standard one for enthalpy changes.*
- *The negative value shows the L.E. is **exothermic**.*
- *This is because it is **bond making** i.e. gaseous ions coming together to make a compound.*

Born-Haber Cycles

Standard enthalpy of formation $\triangle H^{\ominus}_{298.f}$:
Elements in their standard state forming 1 mole of a compound under standard conditions.

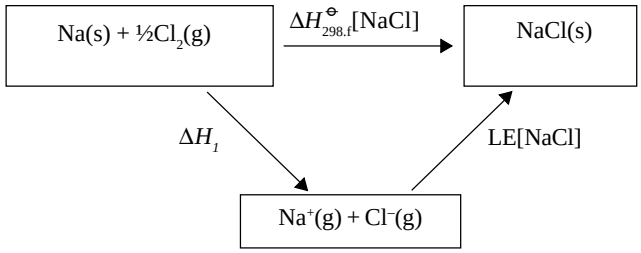
The Born-Haber cycle is based on Hess's Law. The general form of the cycle is:



Using Hess's Law: $\triangle H_1 + LE = \triangle H^{\ominus}_{298.f}$

It is $\triangle H_1$ that is a composite of various terms that need to be written out in full: elements $\rightarrow$ gaseous atoms $\rightarrow$ gaseous ions

Example 1. The Born-Haber Cycle for NaCl



ΔH_1 is made up of the following 4 parts:

$$Na(s) \xrightarrow{\Delta H^{\ominus}_{at}} Na(g) \xrightarrow{1^{st}\ I.E.} Na^+(g)$$

$$\tfrac{1}{2}Cl_2(g) \xrightarrow{\Delta H^{\ominus}_{at}} Cl(g) \xrightarrow{1^{st}\ E.A.} Cl^-(g)$$

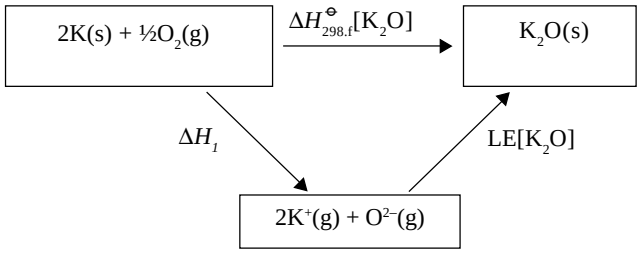
I.E. = ionisation energy E.A. = electron affinity

So, in full, Hess's law gives:

$$L.E.[NaCl] + \Delta H^{\ominus}_{at}[Na(s)] + \Delta H^{\ominus}_{at}[\tfrac{1}{2}Cl_2(g)] + 1^{st}\ I.E.[Na] + 1^{st}\ E.A.[Cl(g)] = \Delta H^{\ominus}_{298.f}[NaCl(s)]$$

Remember *- In practice the ΔH_1 is dealt with separately to give a single numerical value from the separate parts. You do not need to write the Hess's law out as above in full so long as elsewhere in the question you show the ΔH_1 in full.*

Example 2. The Born-Haber Cycle for K_2O.



$$L.E. + \Delta H_1 \rightarrow \Delta H^{\ominus}_{298.f}$$

ΔH_1 is made up of the following 5 parts:

$$2K(s) \xrightarrow{2 \times \Delta H^{\ominus}_{at}} 2K(g) \xrightarrow{2 \times 1^{st}\ I.E.} 2K^+(g)$$

$$\tfrac{1}{2}O_2(g) \xrightarrow{\Delta H^{\ominus}_{at}} O(g) \xrightarrow{1^{st}\ E.A.} O^-(g) \xrightarrow{2^{nd}\ E.A.} O^{2-}(g)$$

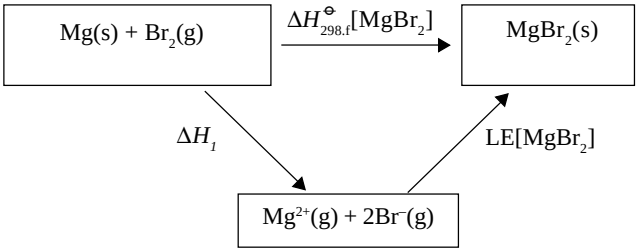
N.B. Notice the need to **double** the values for K because **2 moles** are involved.

Exam Hint*: - Since we are dealing with an ionic solid, ΔH_1 will always involve the enthalpies of atomisation (i.e. converting each element to gaseous ions) and appropriate ionisation energy(ies) and electron affinity(ies) to convert to ions.*

Marks are often lost be ignoring the multiples of each of these required. In particular, note $O_2(g) \rightarrow 2O(g)$ $\Delta H = 2 \times \Delta H^{\ominus}_{at}$ since two moles of gaseous atoms are formed.

Accurate knowledge of definitions is therefore vital for success.

Example 3. The Born-Haber Cycle for $MgBr_2$



$$L.E. + \Delta H_1 \rightarrow \Delta H^{\ominus}_{298.f}$$

ΔH_1 is made up of the following 5 parts:

$$Mg(s) \xrightarrow{\Delta H^{\ominus}_{at}} Mg(g) \xrightarrow{1^{st}\ I.E.} Mg^+(g) \xrightarrow{2^{nd}\ I.E.} Mg^{2+}(g)$$

$$Br_2(g) \xrightarrow{2 \times \Delta H^{\ominus}_{at}} 2Br(g) \xrightarrow{2 \times 1^{st}\ E.A.} 2Br^-(g)$$

N.B. Note the **doubling** of the values for Br_2 because the definitions are all based on 1 mole, and here there are 2 moles.

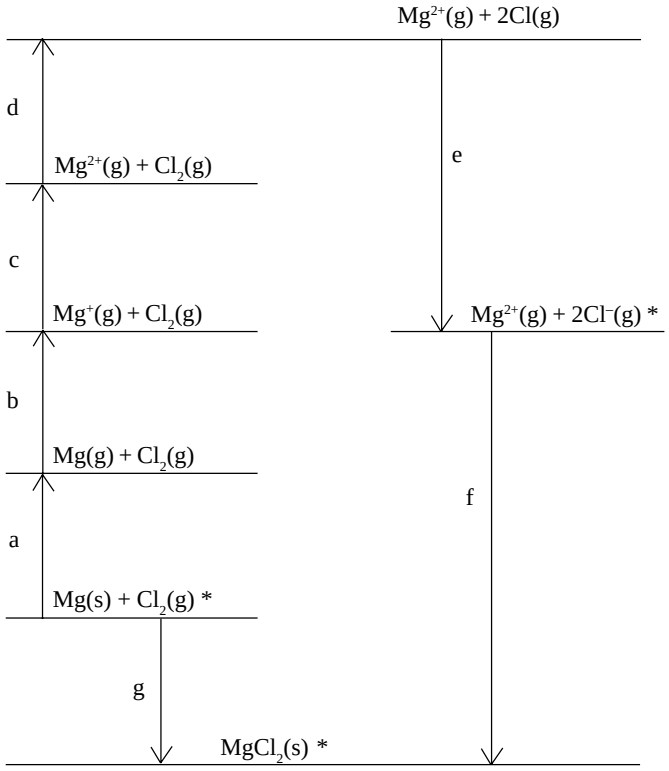
For further practice on writing Born-Haber cycles go to question 3

Enthalpy level diagrams

Another way of presenting Born-Haber cycles is as enthalpy level diagrams.

In these the direction of arrows indicate exothermic (↓) or endothermic (↑)

Look at the following example:



Compare the cycle we have been using with the parts labelled with an * - can you see the link? The * indicates elements, ionic solid and gaseous ions as in the previous form of the cycle. Factsheet 29 covers how to use these diagrams to answer questions.

For further practice on enthalpy diagrams go to question 4.

Trends in L.E. values

Look at the following series of L.E. values (Table 1).

***Exam Hint**: - Candidates may be:*
- *asked to calculate L.E. values via a Born-Haber cycle*
- *given theoretical values of L.E. and asked why they are different*

Table 1. L.E. Values

Series (A)	LE/kJmol^{-1}	Series (B)	LE/kJmol^{-1}	Series (C)	LE/kJmol^{-1}
NaF	-902	$Mg(OH)_2$	-2382	Li_2O	-2814
NaCl	-771	$Cl(OH)_2$	-2093	Na_2O	-2478
NaBr	-733	$Sr(OH)_2$	-1895	K_2O	-2232
NaI	-684	$Ba(OH)_2$	-1768	Rb_2O	-2161

In all three series A, B and C the L.E. values become less exothermic down the Groups 1 and 2. Why is this?

As any metallic group is descended the **cations become larger** and so the **charge density decreases** – this is the cause of the L.E. values becoming less exothermic.

L.E. values are **exothermic** because of **bond making** when the gaseous ions come together to make the ionic solid,

$$M^+(g) + X^-(g) \rightarrow MX(s)$$

The ions are attracted together because of their opposite electrostatic charges, and the stronger the attraction between them the more energy is released.

If you compare series A with C, then C is larger because more ions are involved so more energy released.

Charges in **charge density** affect the value of L.E.

Experimental and Theoretical L.E. Values

The L.E. values calculated by the Born-Haber cycle are based upon values for I.E, E.A, $\triangle H_f^{\ominus}$ and $\triangle H_{at}^{\ominus}$ found by experimentation. These L.E. values are '**experimental**'.

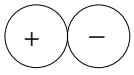
However, because L.E. is about charged spherical ions coming together it is possible to calculate a **theoretical** L.E. value based on the attractive charges involved and the distribution of charge on the spheres (Table 2.)

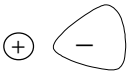
Table 2. Theoretical and experimental L.E. values

	Theoretical L.E./ kJ mol^{-1}	Experimental L.E./ kJ mol^{-1}
NaCl	766	776
NaBr	730	741
AgCl	767	890
AgBr	759	878

NaCl and NaBr show good agreement, the silver salts do not. Why?

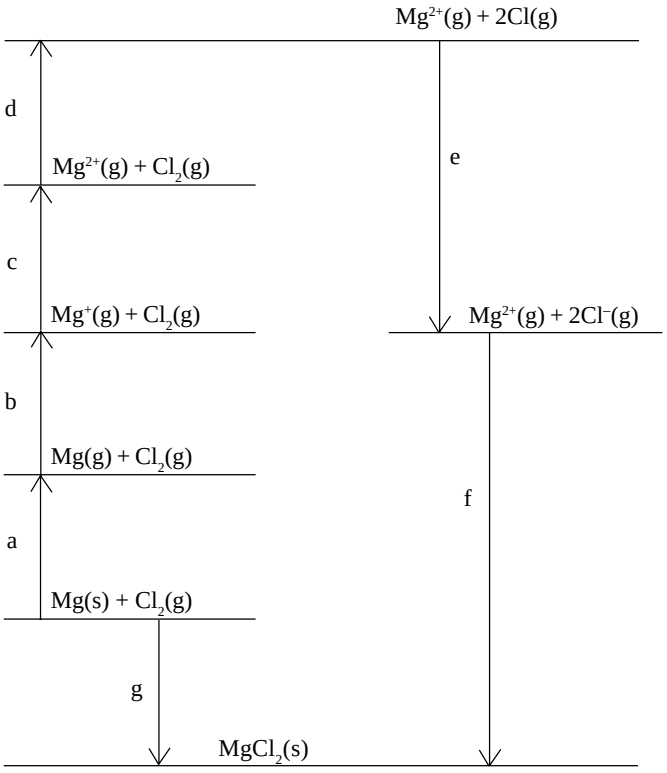
Differences in theoretical and experimental LE values indicate the level of distortion of the anion ie. the degree of polarisation of the anion

Good Agreement both ions are spherical i.e. 

Poor Agreement the anion is distorted and so polarisation has taken place i.e. 

Questions

1. Write the equation for the standard enthalpy of atomisation for the following elements:
   a) $\triangle H_{298.at.}^{\ominus}$ [½I_2(s)]
   b) $\triangle H_{298.at.}^{\ominus}$ [Hg (l)]
   c) $\triangle H_{298.at.}^{\ominus}$ [Zn(s)]
   d) $\triangle H_{298.at.}^{\ominus}$ [½N_2(g)]
2. Write the equation for the Lattice Enthalpy of the following compounds:
   a) ZnO(s)
   b) K_2S(s)
   c) $SrCl_2$(s)
   d) CsF(s)
3. Write the Born-Haber cycle for the following compounds:
   a) ZnI_2(s)
   b) SrO(s)
   c) $CaCl_2$(s)
4. a) Identify each of the enthalpy terms labelled a to g.
   b) In terms of letters a to g what is the Hess's Law cycle?

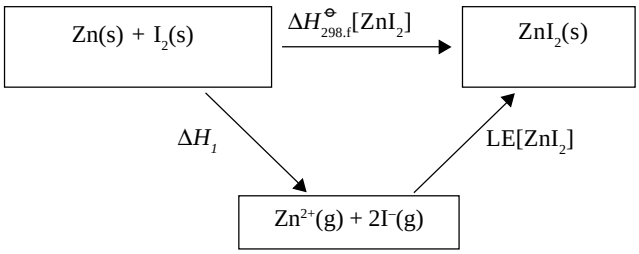


Answers

1. a) $\frac{1}{2} I_2 (s) \rightarrow I(g)$
   b) $Hg (l) \rightarrow Hg(g)$
   c) $Zn (s) \rightarrow Zn(g)$
   d) $\frac{1}{2}N_2 (g) \rightarrow N(g)$

2. a) $Zn^{2+} (g) + O^{2-} (g) \rightarrow ZnO(s)$
   b) $2K^{+} (g) + S^{2-} (g) \rightarrow K_2S(s)$
   c) $Sr^{2+} (g) + 2Cl^{-} (g) \rightarrow SrCl_2(s)$
   d) $Cs^{+} (g) + F^{-} (g) \rightarrow CsF(s)$

3. a)

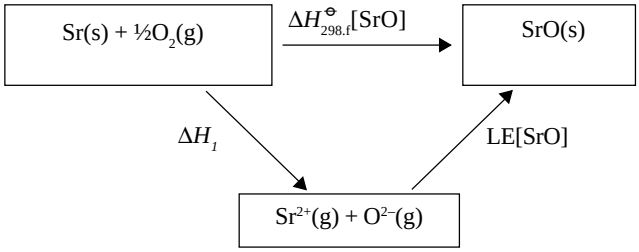


$\triangle H_1$

$Zn(s) \xrightarrow{\triangle H_{at}^{\ominus}} Zn(g) \xrightarrow{1^{st}\ I.E.} Zn^{+}(g) \xrightarrow{2^{nd}\ I.E.} Zn^{2+}(g)$

$I_2(g) \xrightarrow{2 \times \triangle H_{at}^{\ominus}} 2I(g) \xrightarrow{2 \times 1^{st}\ E.A.} 2I^{-}(g)$

b)

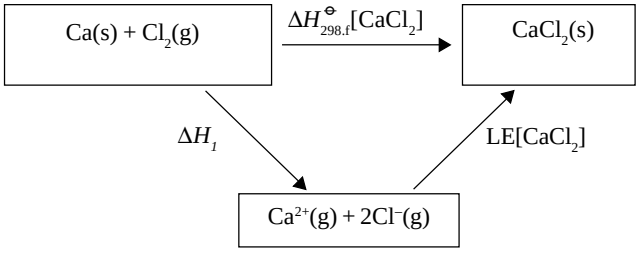


$\triangle H_1$

$Sr(s) \xrightarrow{\triangle H_{at}^{\ominus}} Sr(g) \xrightarrow{1^{st}\ I.E.} Sr^{+}(g) \xrightarrow{2^{nd}\ I.E.} Sr^{2+}(g)$

$\frac{1}{2}O_2(g) \xrightarrow{\triangle H_{at}^{\ominus}} O(g) \xrightarrow{1^{st}\ E.A.} O^{-}(g) \xrightarrow{2^{nd}\ E.A.} O^{2-}(g)$

c)

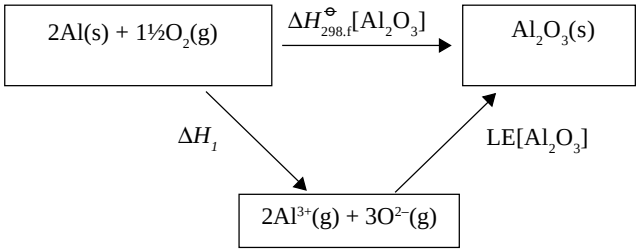


$\triangle H_1$

$Ca(s) \xrightarrow{\triangle H_{at}^{\ominus}} Ca(g) \xrightarrow{1^{st}\ I.E.} Ca^{+}(g) \xrightarrow{2^{nd}\ I.E.} Ca^{2+}(g)$

$Cl_2(g) \xrightarrow{2 \times \triangle H_{at}^{\ominus}} 2Cl(g) \xrightarrow{2 \times 1^{st}\ E.A.} 2Cl^{-}(g)$

c)



$\triangle H_1$

$2Al(s) \xrightarrow{2 \times \triangle H_{at}^{\ominus}} 2Al(g) \xrightarrow{2 \times 1^{st}\ I.E.} 2Al^{+}(g) \xrightarrow{2 \times 2^{nd}\ I.E.} 2Al^{2+}(g) \xrightarrow{2 \times 3^{rd}\ I.E.} 2Al^{3+}(g)$

$1\frac{1}{2}O_2(g) \xrightarrow{3 \times \triangle H_{at}^{\ominus}} 3O(g) \xrightarrow{3 \times 1^{st}\ E.A.} 3O^{-}(g) \xrightarrow{3 \times 2^{nd}\ E.A.} 3O^{2-}(g)$

4. a) a = $\triangle H_{at}^{\ominus}[Mg(s)]$

   b = 1^{st} I.E.[Mg]

   c = 2^{nd} I.E.[Mg^{+}]

   d = $2 \times \triangle H_{at}^{\ominus}[\frac{1}{2}Cl_2(g)]$

   e = 2×1^{st}E.A.[Cl]

   f = L.E.[$MgCl_2$]

   g = $\triangle H_f^{\ominus}[MgCl_2]$

   b) a + b + c + d + e + f = g

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