Chem Factsheet

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Improve Your Marks:
A2 Energetics- Born-Haber Cycles

This Factsheet aims to give you tips to help improve your marks when answering A2 Energetics questions about Born-Haber cycles. The areas covered are:-

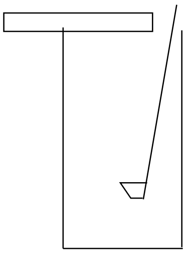
- A check of your understanding about the formation of an ionic compound
- Born-Haber Cycles
- Defining Born-Haber Cycle terms
- Getting each point right in the exam
- Applying the knowledge

Check your understanding about the formation of an ionic compound

Sodium and chlorine

When a piece of hot sodium metal is lowered into a gas jar of chlorine, a violent reaction takes place and spots of a white substance are spattered inside the jar.

Explain as fully as you can what is happening in the gas jar.



Check your answer against the full answer at the end of the factsheet.

Background to the answer
How much detail did you include? Read the answer - a lot of processes occur in a very short period of time in the reaction:-

$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

The product is an ionic lattice – a 3-D crystalline solid consisting of millions of sodium and chloride ions packed in a 1:1 ratio. The "ionic bond" formed between them holds the lattice together. The bond is multi-directional – the charge on ions is all over, so isn't directed towards one specific ion of opposite charge. This makes the strength of ionic bonds much harder to study – where do you start? How many ions should be included? On what basis should comparisons be made? It is difficult to answer these questions by experiment. Instead, chemists investigate, measure and compare ionic bond strength and ionic compound formation using *Born-Haber energy cycles*.

Born-Haber Cycles
Born-Haber Cycles enable us to calculate the **lattice enthalpy change** (**ΔH_L**) for ionic solids which gives an indication of the overall strength and nature of the ionic bonding in the compound. The cycles were developed around 1917 by Max Born and Fritz Haber, two scientists famous for other work: Max Born contributed to our understanding of atomic structure and Fritz Haber developed the "Haber-Bosch Process" (now usually called the Haber Process) for making ammonia.

The **lattice *dissociation* enthalpy change** (ΔH_L) is defined as the enthalpy change occurring when 1 mole of *solid ionic lattice* is *separated* into its gaseous ions under standard conditions of temperature and pressure.

e.g. $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

Conversely, the **lattice *formation* enthalpy change (also ΔH_L)** is defined as the enthalpy change occurring when 1 mole of *solid ionic lattice* is *formed* from its gaseous ions under standard conditions of temperature and pressure.

e.g. $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

Be sure you know which of these definitions is favoured by your specification. They are equal in magnitude but opposite in sign. *Lattice dissociation is always endothermic* because bonds are being broken whereas l*attice formation is always exothermic* because bonds are being formed.
e.g. $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$; + 780 kJ $mole^{-1}$

but $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$; - 780 kJ $mole^{-1}$

In either case, the magnitude indicates the strength of the ionic bonding; the larger the value the stronger the ionic bonding.

If anything, *dissociation is the favoured definition* because it is parallel to the definitions of bond dissociation energy and mean bond enthalpy as applied to covalent bonds.

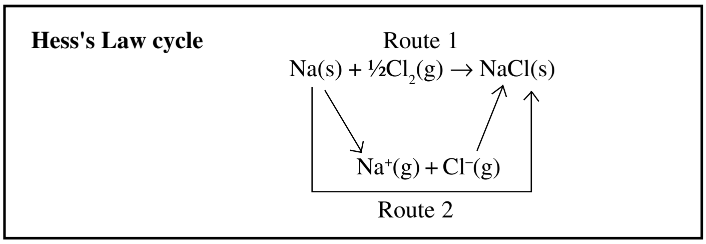
Born-Haber Cycles apply Hess's Law (see FactSheet 98 Improve your marks: AS Energetics). Two differences between a standard Hess's Law cycle and a Born-Haber cycle are:-

1. Born-Haber cycles are presented vertically so they look different. This is a convention arising because of point 2.
2. Born-Haber cycles have a lot more component parts than most Hess's Law cycles.

To illustrate the points, we will use a Born-Haber cycle for the formation of sodium chloride (look back at the starting question and its answer).

The enthalpy change for the formation of sodium chloride can be determined by experiment and the enthalpy changes of the separate steps involved in making ions from the elements and reacting them together can also be measured. This means we can set up the following energy diagram:-

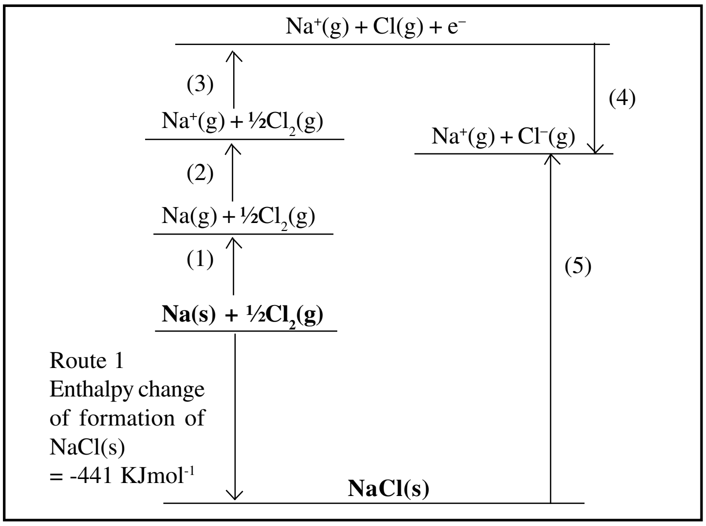
This should look familiar – it's simply a Hess's Law cycle.



Route 1 is direct, but can be measured. Route 2 goes through many steps each of which can be measured *except for the lattice enthalpy*. The enthalpy changes for Routes 1 and 2 must be equal. If we know all the other enthalpy changes of the steps involved in creating the gaseous ions (route 2) and the enthalpy change involved in forming the lattice from the elements (route 1), we can calculate the lattice enthalpy for sodium chloride (part of route 2).

This Hess's Law cycle is shown opposite in a Born-Haber cycle format. The bold parts are the Hess's Law cycle components. The starting point, the chemical elements in their standard states, is on the left-hand side. Usually, endothermic changes are placed on the left, while exothermic changes are on the right. The only exception is the enthalpy change of formation (**route 1**), which can be either exo- or endothermic, and is also shown on the left. **Route 2** is made up of all the other enthalpy changes added together.

Born-Haber cycle



The components for route 2 are:-

Endothermic changes: (1) Atomisation enthalpy of sodium
(2) First Ionisation enthalpy of sodium
(3) Atomisation enthalpy of chlorine

Exothermic changes: (4) Electron affinity of chlorine
(5) Lattice dissociation enthalpy of NaCl

We will refer to these numbered points in the next sections.

Defining Born-Haber cycle terms

No.	Term	Definition	Symbol	Sign
1	Atomisation enthalpy (*For solids* this is also known as the *enthalpy change of sublimation*)	The standard enthalpy change occurring when *1 mole* of *gaseous* atoms is formed from 1 mole of atoms in its *standard state* e.g. Na(s) → Na(g)	$\Delta H^{\ominus}_{at}$ $\Delta H^{\ominus}_{sub}$	ALWAYS +ve
2	First ionisation enthalpy	The standard enthalpy change occurring when 1 mole of *unipositive* ions is formed from 1 mole of *gaseous* atoms e.g. Na (g) → Na^+(g) + e^-	$\Delta H^{\ominus}_{i1}$	ALWAYS +ve
3	Atomisation enthalpy *(For diatomic gases* this is also HALF of the bond dissociation enthalpy)	The standard enthalpy change occurring when 1 mole of *gaseous atoms* is formed from the element in its standard state e.g. ½ Cl_2 (g) → Cl (g)	$\Delta H^{\ominus}_{at}$ $\frac{1}{2}\Delta H^{\ominus}_{D}$	ALWAYS +ve
4	First Electron affinity	The standard enthalpy change occurring when 1 mole of *electrons* reacts with 1 mole of gaseous atoms to produce 1 mole of gaseous *1- ions* e.g. Cl (g) + e^- → Cl^-(g)	$\Delta H^{\ominus}_{ea(1)}$	ALWAYS –ve
5	Lattice **dissociation** enthalpy	The standard enthalpy change occurring when *1 mole* of *solid ionic lattice* is *separated* into its gaseous ions e.g. NaCl (s) → Na^+ (g) + Cl^-(g)	$\Delta H^{\ominus}_{L}$	ALWAYS –ve

First electron affinities are always exothermic but second electron affinities are always endothermic because work needs to be done to overcome the repulsions between the added electron and the 1- ion.
e.g. O^-(g) + e^- → O^{2-}(g) ; + 798 kJ mol^{-1}

Exam Hint:- *Questions often refer simply to a "lattice enthalpy". Strictly, "lattice enthalpy" is defined in two different ways depending on whether the ionic lattice is being formed or broken up as described earlier. Use the sign of the enthalpy change to decide which is being used. If lattice formation ethalpy change is given, the arrow in the previous diagram will need to be reversed.*

Definitions are normally worth 2 marks each in an exam question. The details of the defined processes are important but "*1 mole*" is essential because the units throughout are "kJmol^{-1}" and you should always refer to a "*standard enthalpy change*" .

Getting each point right in the exam

Next we will take each point from an exam perspective. What do you need to look for?

No.	Name and where to find it	Do's and Don'ts	Remember to
1	**Atomisation enthalpy of a solid** First step going upwards from the element in its standard state	**Don't** call it "enthalpy of vapourisation". This scores no marks.	Include "*standard state*" in a definition. This scores 1 mark. Include state symbols (s) and (g) when drawing a BHC.
2	**Ionisation enthalpy** Second step going upwards on the left-hand side.	**Do** check the charge on the ion! Magnesium and calcium will be 2+. This will require you to **use $\Delta H^{\ominus}_{i1} + \Delta H^{\ominus}_{i2}$**	Check: Some BHC diagrams combine first and second ionisation energies together, others show them separately.
3	**Atomisation enthalpy of a diatomic gas.** Final left-hand step going to the top of the BHC diagram.	**Do** check the symbols: " ½Cl_2" and "Cl_2" are possible	use **+121 kJ mol^{-1}** in a calculation using **½Cl_2** (e.g. NaCl(s)) but **2(+121) kJ mol^{-1}** in a calculation using **Cl_2** (e.g. $MgCl_2$(s)).
4	**Electron affinities** First step down on the right hand side Normally chlorine but other elements such as sulphur may be used	**Do** check the number of atoms**:** Cl and 2Cl are possible **Do** check the charge on the final ion: e.g. sulphur is S^{2-}. This will require you to **use $\Delta H^{\ominus}_{ea1} + \Delta H^{\ominus}_{ea2}$**	use **-349 kJ mol^{-1}** in a calculation using **Cl** (e.g. NaCl(s)) but use **2(-349) kJ mol^{-1}** in a calculation using **2Cl** (e.g. $MgCl_2$(s)). Try to memorise these values – you may be asked to calculate them, so you will know the right answer. Check: a second electron affinity is *endothermic* due to repulsion
5	**Lattice dissociation enthalpy** Lowest step on right hand side	**Do** check you use a **positive** value	Compare values: highest values imply the strongest ionic bonds

Applying the knowledge

Let's use figures for the sodium chloride BHC diagram to illustrate the kinds of questions examiners like to ask. The numbers and names in the table below give the data we need and correspond with the BHC diagram above.

No.	Name	Value / kJmol^{-1}
1	Atomisation enthalpy of sodium	+ 107
2	First ionisation enthalpy of sodium	+496
3	Atomisation enthalpy of chlorine	+121
4	Electron affinity of chlorine	-349
5	Lattice dissociation enthalpy	+786

> ***Exam Hint:-*** *When applying Hess's Law to such a cycle, it is often useful to use "sum of clockwise ΔH = sum of anti-clockwise ΔH" to help you get the arithmetic correct.*

- **Calculate the lattice dissociation enthalpy for sodium chloride**

  Route 1 = Route 2
  $-411 + \Delta H_{LE} = +107 + 496 + 121 + (-349)$
  $\mathbf{\Delta H_{LE} = +786\ kJmol^{-1}}$

- **Calculate the first electron affinity for chlorine**

  Route 1 = Route 2
  $-411 + 786 = +107 + 496 + 121 + \Delta H_{ea}$
  $\Delta H_{ea} = -411 + 786 - 107 - 496 - 121$
  $\mathbf{\Delta H_{ea} = -349\ kJmol^{-1}}$

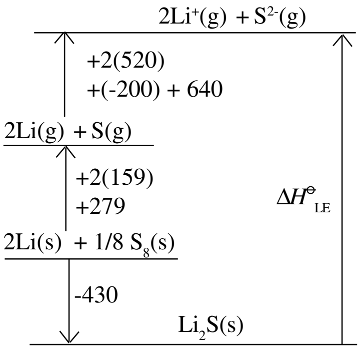
> ***Remember:***
> - *Look for the two routes on a BHC diagram. The "clockwise route" and the "anticlockwise route".*
> - *Check the sign of your answer – the correct sign is vital and worth 1 mark! Use the definitions table to help you learn what the signs should be.*
> - *State the units – this is good practice, even though marks may not be awarded for them.*
> - *Note that answers can vary within +/- 2kJmol^{-1} – this is due to rounding up and down and use of different databook values.*

Related Data:

Element	$\Delta H^{\ominus}_{at}$	Element	$\Delta H^{\ominus}_{I1}$	$\Delta H^{\ominus}_{I2}$	$\Delta H^{\ominus}_{I3}$	$\Delta H^{\ominus}_{ea1}$	$\Delta H^{\ominus}_{ea2}$
Li(s)	+159	Li(g)	+520				
Na(s)	+107	Na(g)	+496				
K(s)	+89	K(g)	+419				
Cs(s)	+76	Cs(g)	+376				
Mg(s)	+148	Mg(g)	+738	+1451			
Ca(s)	+178	Ca(g)	+590	+1145			
Al(s)	+326	Al(g)	+578	+1817	+2745		
½F_2(g)	+79	F(g)				-328	
½Cl_2(g)	+121	Cl(g)				-349	
½Br_2(l)	+112	Br(g)				-325	
½I_2(s)	+107	I(g)				-295	
½O_2(g)	+249	O(g)				-141	+798
1/8S_8(s)	+279	S(g)				-200	+640

Example 2

Calculate the lattice dissociation energy of lithium sulphide given that its standard enthalpy of formation is -430 kJ mol^{-1}.



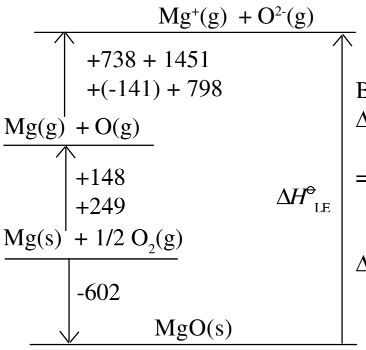
By Hess's Law:
$\Delta H^{\ominus}_{LE}[Li_2S(s)] + (-430)$

$= +279 + 2(159) + (-200)$
$+640 + 2(520)$

$\Delta H^{\ominus}_{LE}[Li_2S(s)] = +2507$ kJ mole^{-1}

Example 3

Calculate the lattice dissociation energy of magnesium oxide given that its standard enthalpy of formation is -602 kJ mol^{-1}.



By Hess's Law:
$\Delta H^{\ominus}_{LE}[MgO(s)] + (-602)$

$= +148 + 249 + (-141) +$
$798 + 738 + 1451$

$\Delta H^{\ominus}_{LE}[MgO(s)] = +3845$ kJ mole^{-1}

Answer to the introductory question

Sodium and chlorine react to form an ionic lattice. In the process, sodium metal is sublimed to sodium gas. In this example, liquid sodium metal is used. In the reaction, sodium atoms lose one electron each becoming sodium ions. Chlorine gas molecules split apart, making chlorine atoms. Each chlorine atom accepts one electron from a sodium atom becoming a chloride ion. The sodium ions and chloride ions come together releasing energy as a solid ionic lattice of sodium chloride forms. This is the white stuff observed at the end of the reaction.

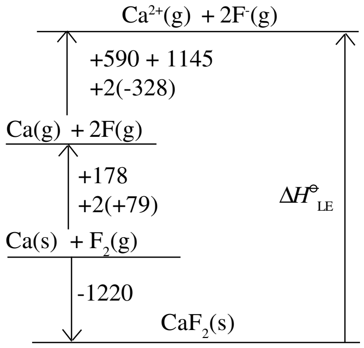
Practice Questions

1. Calculate the lattice dissociation energy of calcium fluoride given that its standard enthalpy of formation is -1220 kJ mol^{-1}.

2. Calculate the lattice dissociation energy of aluminium oxide given that its standard enthalpy of formation is -1676 kJ mol^{-1}.

Answers

1.

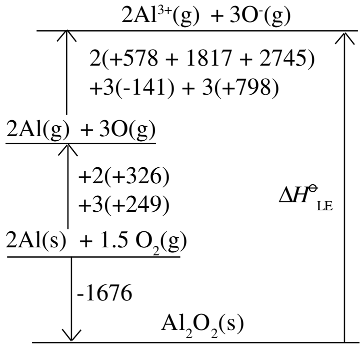


By Hess's Law:
$\Delta H^{\ominus}_{LE}[CaF_2(s)] + (-1220)$

$= +178 + 2(79) + 2(-328)$
$+590 + 1145$

$\Delta H^{\ominus}_{LE}[CaF_2(s)] = +2635$ kJ mole^{-1}

2.



By Hess's Law:
$\Delta H^{\ominus}_{LE}[Al_2O_3(s)] + (-1676)$

$= +2(326) + 3(249) + 2(+578)$
$+2(+1817) + 2(+2745)$
$+3(-141) + 3(+798)$

$\Delta H^{\ominus}_{LE}[Al_2O_3(s)] = +15326$ kJ mole^{-1}

Acknowledgements: *This Factsheet was researched and written by Vanessa Kind.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***