Chem Factsbeet



January 2002 Number 29 Answering Questions On Born-Haber Cycles

To succeed in this topic you need to thoroughly understand how to write Born-Haber cycles (covered in Factsheet No. 28)

After working through this Factsheet you will know and understand:

- how to convert Born-Haber cycles into numerical answers given the relevant data;
- how the data given is used to test the understanding of definitions by candidates;
- the relationship between the marks for a question and the balance between writing the cycle and calculating an answer;
- the use of enthalpy level diagrams to test the understanding of candidates of definitions and Born-Haber cycles.

Questions on Enthalpy Level Diagrams

There are two types of questions on these diagrams:

1. Identifying enthalpy changes

2. Calculating a numerical answer from given values on a diagram

1. Identifying enthalpy changes



Example 1

Question: Identify the stages a – g

Method

For each arrow look to see **what has changed**. It is then a matter of deciding **which definition** it matches and **how many moles**.

Answer:

a =	gaseous ions to ionic solid	=	L.E.
b =	$2Br(g) \rightarrow 2Br(g)$	=	2×1^{st} E.A.
c =	$Br_2(g) \rightarrow 2Br(g)$	=	$2 \times \triangle H_{at}^{\Theta} [\frac{1}{2} Br_2]$
d =	$Zn^{+}(g) \rightarrow Zn^{2+}(g)$	=	2^{nd} I.E.
e =	$Zn(g) \rightarrow Zn^{+}(g)$	=	1 st I.E.
f =	$Zn(s) \rightarrow Zn(g)$	=	$\triangle H_{\rm at}^{\Theta}[{\rm Zn}({\rm s})]$
g =	$elements \rightarrow compound$	=	$\triangle H_{\rm f}^{\bar{\Phi}}[{\rm ZnBr}_2({\rm s})]$

Example 2

Question: How are a – g linked by Hess's Law?

 $\triangle H_1 + \text{L.E.} = \triangle H_f^{\Theta}$

Method: Identify on the diagram: elements, compound and gaseous ions



So:

Answer: f + e + d + c + b + a = g

Or alternatively, "follow the diagram round" - starting and finishing with the elements. If you go in the **same** direction as an arrow, you **add** the corresponding value; if in the **opposite** direction, **subtract** the value. Finally, equate to zero: f + e + d + c + a - g = 0

2. Calculating a numerical answer given all the other values and the diagram

Question What is the value of *X*?

Method: Either convert to an enthalpy cycle:

Identify each of: elements, compound and gaseous ions, then draw the diagram: $\wedge H^{\oplus}$



Identify the components in the diagram and put in the values.

Answer
$$-635 = +192 + 590 + 1150 + 250 + X - 351$$

 $-635 = X - 1330$
 $X = +1330 - 635 = +695 \text{ kJ mol}^{-1}$

Or follow the diagram round, starting and finishing with the elements: 192 + 590 + 1150 + 250 + X + (-3512) - (-635) = 0

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Note: The direction of the arrow tells us whether to add or subtract. We are going in the direction of the arrow for the -3512, so we add (-3512).

$$X - 695 = 0$$
 so $X = +695$ kJmol⁻¹

For practice on this type of calculation, go to question 1.

Further calculations using Borh-Haber Cycles

All of these use the enthalpy cycle below (or the enthalpy level diagrams - whichever you prefer). You may be required to find enthalpies of formation, electron affinities etc, but the approach in each case is identical.



Method

- 1. Draw the Born-Haber Cycle including all parts of $\triangle H_1$, which will include enthalpies of atomisation and appropriate ionisation energies and electron affinites
- 2. Substitute the values given
- 3. Calculate the 'missing' value and so the answer

Exam Hint: - Candidates should be aware that **all** the definitions for *I.E., E.A.,* $\Delta H_t^{\oplus} \Delta H_t^{\ominus}$ and *L.E.* are based on **1 mole**. Watch out for the following 'data traps' that are used to test whether you know the definitions are for 1 mole

- a) Cl₂(g) → 2Cl⁻(g) ΔH = + 244 kJmol²
 i.e. you have been given 2 x ΔH_{at} [½Cl₂]. The question means you have to use +244/2 if the cycle uses ½Cl₂ → Cl(g)
- b) $Mg(g) \rightarrow Mg^{2+}(g) \Delta H = + 2289 \text{ kJmol}^1$ i.e. you have been given the **total** of the 1st I.E. + 2nd I.E. for Mg
- *c)* Suppose you are asked to find the E.A. of Cl from a cycle involving $MgCl_2(s)$.

When you put in all the values you find the answer for $2Cl(g) \rightarrow 2Cl(g)$. The answer needs \div 2 because E.A. is for 1 mole! This is a common way of catching out candidates.

Look out for these 'data traps' as you attempt Question 3. onwards – they are marked in the answers in order to help you out.



 $\triangle H_1$

$$Na(s) \xrightarrow{\Delta H_{at}^{\Theta}} Na(g) \xrightarrow{1^{st} I.E.} Na^{+}(g)$$

$$\frac{1}{2} \operatorname{Cl}_{2}(g) \xrightarrow{\Delta H_{\mathrm{at}}^{\Theta}} \operatorname{Cl}(g) \xrightarrow{1^{\mathrm{st}} \mathrm{E.A.}} \operatorname{Cl}(g)$$
$$\triangle H_{\mathrm{f}}^{\Theta} = \Delta H_{1} + \mathrm{L.E.}$$

Question: What is the L.E. for NaCl(s)?

 $\triangle H_{f}^{\Theta}[\text{NaCl}(s)] = -411 \text{ kJmol}^{-1} \qquad \triangle H_{at}^{\Theta}[\text{Na}(s)] = +109 \text{ kJmol}^{-1}$

 $\Delta H_{at}^{\Theta}[1/2Cl_2(g)] = +121 \text{ kJmol}^{-1}$ 1st E.A.Cl = -364 kJmol^{-1}

 1^{st} I.E. Na = +494 kJmol⁻¹

$$-411 = +109 + 121 - 364 + 494 + L.E.$$

L.E. =
$$-771 \text{ kJmol}^{-1}$$

iagrams Questions

1. a) Identify s, t, u, v, w, x and y in the following cycle:



b) What is the relationship between s - x?

You will need the following data to answer questions 2 to 7 (all values in kJ mol⁻¹):

$Cl_2(g) \rightarrow 2Cl(g) = -242$	$Cl(g) \rightarrow Cl^{-}(g) = -364$
$\frac{1}{2}O_2(g) \to O(g) = +249$	$O(g) \rightarrow O^{-}(g) = -141$
$O^{-}(g) \rightarrow O^{2-}(g) = +798$	$K(s) \rightarrow K(g) \ = +90$
$K(g) \rightarrow K^{\scriptscriptstyle +}(g) = +418$	$Mg(s) \rightarrow Mg(g) = +148$
$Mg(g) \rightarrow Mg^+(g) = +738$	$Mg^{\scriptscriptstyle +}(g) \to Mg^{\scriptscriptstyle 2+}(g) = +1451$
$\frac{1}{2}Br_2(g) \rightarrow Br(g) = +112$	$Br(g) \rightarrow Br^{-}(g) = -325$
$Zn(s) \rightarrow Zn(g) = +131$	$Zn(g) \rightarrow Zn^{2+}(g) = +2639$
$I_2(g) \rightarrow 2I(g) = +214$	$I(g) \rightarrow I^{-}(g) = -314$
$Sr(s) \rightarrow Sr(g) = +164$	$Sr(g) \rightarrow Sr^{+}(g) = +550$
$Sr^{+}(g) \rightarrow Sr^{2+}(g) = +1064$	$Ca(s) \rightarrow Ca(g) = +178$
$Ca(g) \rightarrow Ca^{2+} = +1735$	$\triangle H_{\rm f}^{\bullet}[{\rm K}_{2}{\rm O}({\rm s})] = -361$
$\triangle H_{\rm f}^{\oplus}[{\rm MgBr}_2({\rm s})] = -524$	L.E. $(ZnI_2)(s) = -2605$
L.E. (SrO) = -3223	$\triangle H_{\rm f}^{\Theta}[{\rm CaCl}_2] = -796$

2. Using the cycle for K_2O below calculate the L.E.



3. Using the cycle for MgBr₂ below calculate the L.E.



- 4. Write the Born-Haber cycle for ZnI_2 and use it to find $\triangle H_f$ [ZnI₂]
- 5. Write the Born-Haber cycle for SrO and use it to find the $\triangle H_{\rm f}$ [SrO]
- 6. What value for the E.A. of chlorine does the Born-Haber cycle for CaCl₂ produce?

For more practice on Born-Haber cycles try questions 2-6

Answers

1. a)
$$s = \Delta H_{f}^{\Theta} [CaBr_{2}]$$

 $u = 2 \times E.A. (Br)$
 $w = 2^{nd} I.E. (Ca^{+})$
 $y = \Delta H_{at}^{\Theta} [Ca]$
 $t = L.E. (CaBr_{2})$
 $v = 2 \times \Delta H_{at}^{\Theta} [\frac{1}{2}Br_{2}]$
 $x = 1^{st} I.E. (Ca)$

- b) s = y + x + w + v + u + t
- 2. L.E. = 1485 kJmol⁻¹
- 3. L.E. = 2435 kJmol⁻¹



 $\triangle H_1$

$Zn(s) \xrightarrow{\Delta H_{at}^{\Theta}} Zn(g)$ +131	$-\underbrace{\overset{1^{st} \text{ I.E.}}{\longleftarrow} \text{Zn}^{+}(g)}_{+2639}$	$\xrightarrow{2^{nd} \text{ I.E.}} Zn^{2+}(g)$
$I_2(s) \xrightarrow{2 \times \Delta H_{at}^{\Theta}}{2I(g)}$	$\frac{2 \times \text{E.A.}}{2 \times -314} \ge 2I^{-}(g)$	

N.B. Notice data changes for I₂ and Zn/Zn²⁺

 $\triangle H_1 = +2356$ $\triangle H_f^{\Theta} = +2356 = 2605$ $= -249 \text{ kJmol}^{-1}$



 ΔH_{1} $Sr(s) \xrightarrow{\Delta H_{at}^{\Theta}} Sr(g) \xrightarrow{1^{st} I.E.} Sr^{*}(g) \xrightarrow{2^{nd} I.E.} Sr^{2+}(g)$

$$\frac{1}{2}O_{2}(g) \xrightarrow{\Delta H_{at}^{\oplus}} O(g) \xrightarrow{1^{st} \text{ E.A.}} O^{-}(g) \xrightarrow{2^{nd} \text{ E.A.}} O^{2-}(g)$$

$$\triangle H_1 = +2684$$

 $\triangle H_{\rm f}^{\oplus} = +2356 - 3223 = -539 \,\rm kJmol^{-1}$





$$\operatorname{Cl}_{2}(g) \xrightarrow{2 \times \Delta H_{at}^{\Theta}} 2\operatorname{Cl}(g) \xrightarrow{2 \times E.A.} 2\operatorname{Cl}(g)$$

N.B. Ca \rightarrow Ca²⁺ is **total value**, and Cl₂ \rightarrow is given for 2 $\times \triangle H_{at}^{\ominus}$ already.

$$\triangle H_1 = +1671 + x$$

- 796 = +1671 + x - 2258

 $\therefore x = -796 - 1671 + 2258 = -209$

but this is $2 \times E.A$, so $-209/2 = -104.5 \text{ kJmol}^{-1}$

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