Chem Factsheet

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Why Students Lose Marks : Born-Haber Calculations

Which of the following statements are true and which are false?

	Statement	True	False
1	The value of ÄH for lattice formation is always negative.		
2	All halides which have an exothermic ΔH_f value exist.		
3	The direction of spontaneous change can always be deduced from the sign of the enthalpy change		
4	The terms energy change, enthalpy change and heat change all mean the same		
5	Electron affinity is always exothermic		
6	Atomisation refers to the formation of a mole of ions from the element.		
7	The lattice enthalpy depends on the charge density on the ions		

If you answered true for the first and last statements, then you are clearly a star student!

If you thought that the fourth statement was true, then in general this would be alright at A level, but when giving definitions or when labelling Born Haber cycles, it is important to understand that **using the term energy change (represented by ΔU) instead of heat or enthalpy change (ΔH) is incorrect**, and should be avoided.

A sound basis for this topic is a good understanding of energy cycles and of Hess's Law in particular. Born Haber cycles are the application of Hess's Law to the formation of ionic compounds.

It is important to remember:

1. **State symbols** are vital for Born Haber cycles and must always be included.
2. **All the steps** must be included.
3. It is important to make sure that the **cycle balances** (in a similar way to when balancing equations). For example one mole of atoms cannot become two moles in moving from one step to the next.
4. **Electrons** being transferred must balance and always be included.
5. **Signs**, especially when doing calculations, as it is easy to make a mistake when adding and subtracting negative numbers. Doing the calculation in stages and using brackets may be a good idea.
6. The **results must be sensible**. The stability of a compound with respect to its elements is greater the more exothermic (negative) the enthalpy of formation from its elements, thus for a compound such as sodium chloride this value must be large and negative to be correct.

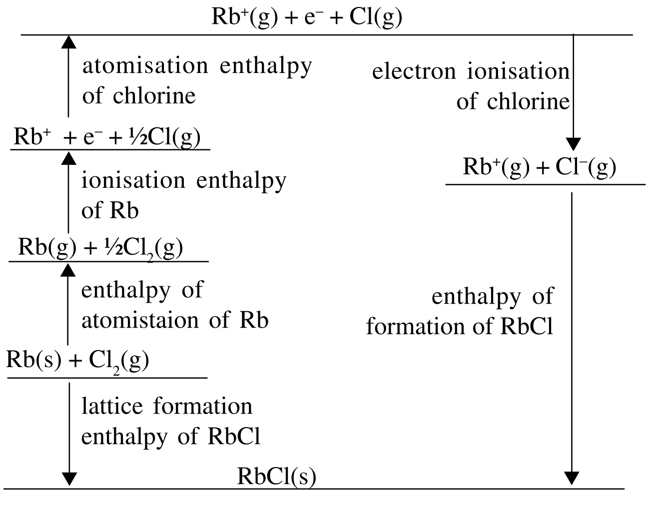
> **Extract from an examiners report:** *"although the question specifically stated that a fully labelled Born Haber cycle was required with symbols for all species, many candidates lost marks when they omitted state symbols, electrons, steps and gave incorrect species"*

In the following worked questions, having read the question carefully, consider the student's answer and see if you can spot any errors **before referring to the comments or mark scheme**.

Sample Student's Worked Question Number 1

(a) Draw a fully labelled Born-Haber cycle for the formation of rubidium chloride from its elements. Include state symbols for all species involved. (4 marks)

Student's Answer to part a):



Comments on this answer

The student **fails to gain any marks** for this cycle for the following reasons:

1. The student has confused the lattice formation enthalpy with the enthalpy of formation of rubidium chloride ➔ **two steps** incorrect!
2. Named the electron affinity of chlorine as electron ionisation, even though the correct name is given in part b of the question!
3. Omitted the ½ before the $Cl_2(g)$ of the enthalpy of formation step.
4. Left out the state symbol after Rb in the ionisation enthalpy step.

This leaves only one step completely correct, which is not credit worthy.

(b) Use the data given to find the first electron affinity of chlorine. (2 marks)

Enthalpy Change	/ kJ mol^{-1}
Enthalpy of formation of rubidium chloride	- 435
Enthalpy of atomisation of rubidium	+ 81
Enthalpy of atomisation of chlorine	+ 122
1st ionisation energy of rubidium	+ 403
Lattice Enthalpy of rubidium chloride	- 690

Student's Answer to part b):

Cycling clockwise: 81 + 122 + 403 + EA - - 690 - 435 gives complete cycle = 0

Thus EA = -(81 + 122 + 403 + 690) + 435 = - 861kJmol^{-1}

Comments on this answer

Although the answer is **clearly incorrect**, due to the student transposing the lattice formation enthalpy with the enthalpy of formation of rubidium chloride, some examining boards may allow consequential marking from part a and so the student might have two marks. However a clever student might decide that -861 is rather high and check his/her energy cycle!

(c) The lattice enthalpy of sodium chloride is more exothermic than that of rubidium chloride. Explain this.

Student's Answer to part c):

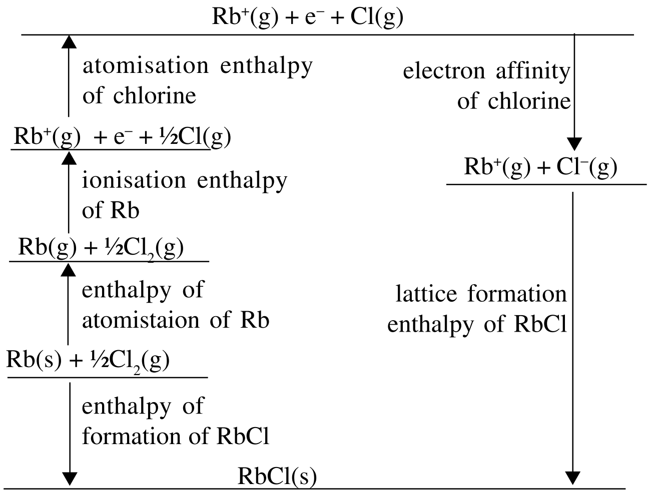
Sodium chloride is extremely stable. For example it is used a lot in cooking and also found in sea water. Its ionic structure is very closely packed, so there is a lot of force between ions.

Comments on this answer

The first two statements are irrelevant. Although the third comes closer to the idea required, it is vague, applies equally to rubidium chloride and sodium chloride, and does not explain the difference ➔ zero marks!

Mark Scheme For Question 1:

(a)



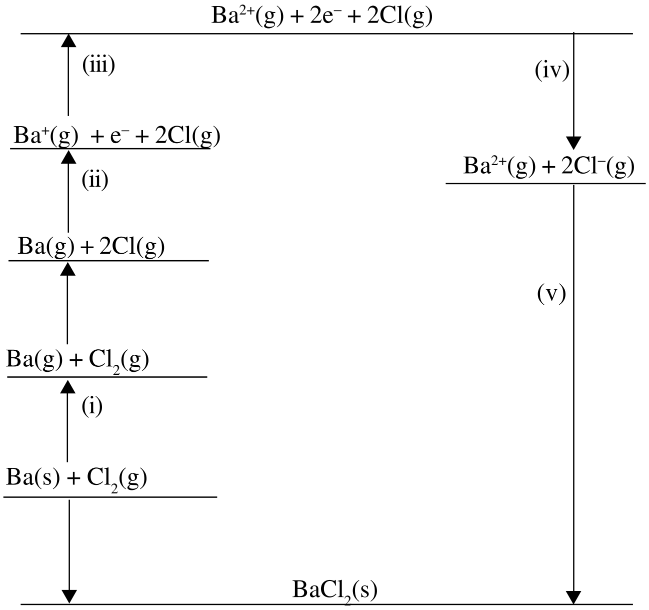
Suitable cycle drawn with 6 steps all clearly and correctly labelled gives 4 marks. 5/4 steps correct gives 3 marks ; 3 correct gives 2 marks ; 2 correct gives 1 mark

(b) Cycling clockwise:
81 + 403 + 122 + EA + (-690) – (-435) = 0
EA = - (81 + 403 +122) + 690 – (+435) (1st mark)
EA of chlorine = - 351 kJmol^{-1} (2nd mark)

(c) The Na^+ ion is smaller than the Rb^+ ion and so the **charge density of the Na^+ is greater** than that of the Rb^+ ion. (1st mark)
This results in the **attractive forces in the NaCl lattice being stronger** than in the RbCl lattice. (2nd mark)

Sample Student's Worked Question Number 2

A Born-Haber cycle for the formation of barium(II) chloride is shown below.



In the spaces below give each of the enthalpy changes (i) to (v) above. Remember to notice the direction of the required enthalpy change and the number of moles of each species involved. (5 marks)

Student's answer:

Enthalpy change (i)...*enthalpy of vaporisation of barium.*
Enthalpy change (ii)...*ΔH atomisation of chlorine.*
Enthalpy change (iii)...*ionisation enthalpy.*
Enthalpy change (iv)...*electron affinity of chlorine.*
Enthalpy change (v)...*lattice breaking enthalpy of* $BaCl_2$.

Comments on this answer

The student fails to score any marks for the following reasons:

(i) Vaporisation should be replaced by 'atomisation or sublimation' which refers to 'forming 1 mol of **gaseous** atoms from the element'.

(ii) The student has failed to realise that 1 mol of atoms is formed from $½Cl_2$. Thus the change referred to is 2 x ΔH_{atom}.

> <u>**Note**</u> In fact it is easy to confuse enthalpy of atomisation with bond energy, especially for **diatomic** gases:
> Atomisation $½Cl_2(g) \rightarrow Cl(g)$ $\Delta H = 121$ kJmol^{-1}
> Bond Energy $Cl_2(g) \rightarrow 2Cl(g)$ $\Delta H = 242$ kJmol^{-1}

(iii) The student fails to specify which ionisation enthalpy is referred to, that is the second.

Note The main point to note is that successive values each refer to the removal of **one** electron. The second ionisation enthalpy refers to the process

$M^+(g) \rightarrow M^{2+}(g) + e^-$

This is NOT $M(g) \rightarrow M^{2+}(g) + 2e^-$

and NOT $M(g) \rightarrow M^+(g) + e^-$

and does NOT have the same numerical value as either of these and so to avoid ambiguity the correct full name must be given.

(iv) The student fails to notice that two moles of chloride ions are formed from two moles of chlorine atoms. The enthalpy change is thus 2 × the electron affinity of chlorine.

(v) The student fails to note that the lattice is being formed, so the lattice formation enthalpy of $CaCl_2$ is the correct answer.

Note Lattice enthalpy for formation (association) is always negative, whereas for lattice breaking (dissociation) the value is positive.

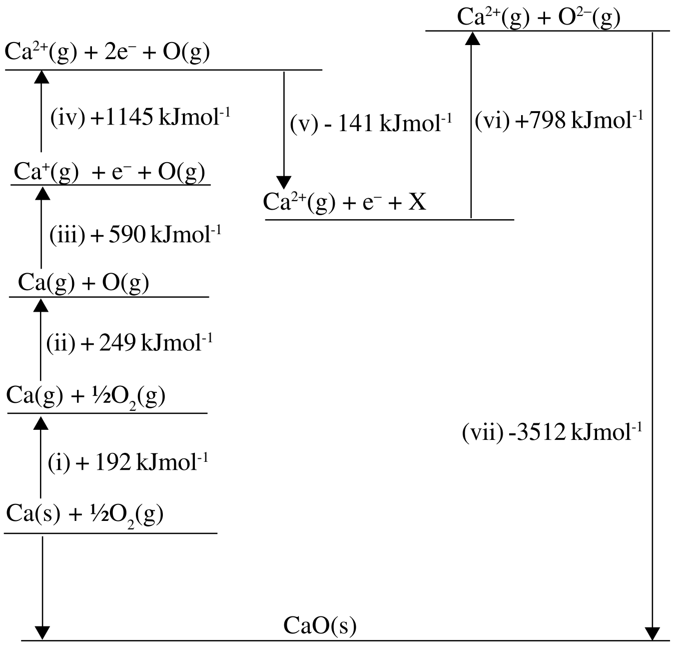
In general these are **common mistakes** which are commented upon by examining boards.

Mark Scheme For Question 2:

(i) Enthalpy of atomisation / sublimation of barium (1 mark)
(ii) 2× enthalpy of atomisation of chlorine (1 mark)
(iii) Second ionisation enthalpy of barium (1 mark)
(iv) 2× electron affinity of chlorine (1 mark)
(v) Lattice formation enthalpy of $BaCl_2$ (1 mark)

Practice Questions

A Born-Haber cycle for the formation of calcium oxide from its elements is shown.



(a) Name the enthalpy change for each of the steps (i) to (vii) above. (7 marks)

(b) Give the full electronic arrangement of the ion O^{2-} (1 mark)

(c) Identify the species X formed in step (v) (1 mark)

(d) Why is step (vi) an endothermic process? (2 marks)

(e) Explain why the enthalpy change for step (iv) is greater than for step (iii) (2 marks)

(f) Use the data given in the cycle to calculate a value for ÄH$_f$CaO (2 marks)

Answers

(a) (i) Enthalpy of atomisation / sublimation of calcium
(ii) Enthalpy of atomisation of oxygen
(iii) First ionisation enthalpy of calcium
(iv) Second ionisation enthalpy of calcium
(v) First electron affinity of oxygen
(vi) Second electron affinity of oxygen
(vii) Lattice formation / association enthalpy of calcium oxide

(b) The electronic arrangement of the ion O^{2-} is $1s^2$ $2s^2$ $2p^6$

(c) O^-

(d) The negative charge of the oxygen O^- ion (1st mark) repels the electron which is being added. (2nd mark)

It is worth noting that although the enthalpies of attaching an electron tend to be negative (an exothermic process), when considering oxygen and sulphur where two electrons are added, whereas the process of adding the first electron is exothermic, the increased electron-electron repulsion makes the second addition strongly endothermic.

(e) The electron is more strongly attracted (1st mark) due to the +1 charge already on the Ca^{1+} (2nd mark) (so less easily removed)

(f) Going clockwise around the cycle:

$+ 192 + 249 + 590 + 1145 - 141 + 798 - 3512 - \Delta H_f CaO = 0$ (1st mark)

$\Delta H_f CaO = - 679 \text{ kJmol}^{-1}$ (2nd mark)

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