

The ΔH of Lattice Enthalpy,

A First and Second Year Blog for the week commencing the 9th February 2020.

(In order to understand some of the ΔH s in this Blog, some thought has to be given to the processes that are involved. Take your time and try to understand what is going on. They often ask questions about ΔH of Lattice Enthalpy in the exams at the end of your Second Year.)

- Please note that the ΔH s on this page are just descriptions and are **NOT** definitions. For a definition I would have had to specify for exactly which species I was calculating the ΔH for one mole of that species, and under what states and under what conditions, etc. **On this page I am NOT doing all that.**
- In order to understand the ΔH of Lattice Enthalpy, you need first to understand a number of other ΔH s. Indeed. There is in fact a huge number of ΔH s.¹ There can be a ΔH for every different *type* of reaction known. For example
 - ΔH_{ie1} = ΔH of First Ionisation Energy.
 - ΔH_{ie2} = ΔH of Second Ionisation Energy (and I could talk about $\Delta H_{ie3}/\Delta H_{ie4}/\Delta H_{ie5}/\Delta H_{ie6}/etc$).
 - ΔH_{ea1} = ΔH of First Electron Affinity Energy.
 - ΔH_{ea2} = ΔH of Second Electron Affinity Energy (and I could talk about $\Delta H_{ea3}/\Delta H_{ea4}/\Delta H_{ea5}/\Delta H_{ea6}/etc$).
 - ΔH_f = ΔH of a Formation reaction.
 - ΔH_c = ΔH of a Combustion reaction.
 - ΔH_n = ΔH of a Neutralisation reaction.
 - ΔH_m = ΔH of a Melting reaction (in making the transition from a solid to a liquid).
 - ΔH_{vap} = ΔH of a Vapourisation reaction (in making the transition from a **liquid to a gas**).
 - ΔH_{sub} = ΔH of a Sublimation reaction (in making the transition from a **solid to a gas**).
 - ΔH_{hyd} = ΔH of Hydration of an ionic substance by water where every **gaseous ion** becomes surrounded by and reacts with molecules of water e.g. $Cl^-(g) + H_2O \rightarrow Cl^-(aq)$. Hydration enthalpies are always negative. The size of/the amount of the hydration enthalpy is influenced by the **charge density** of the metal cation involved e.g. Mg^{2+} has a greater charge density than Na^+ , therefore the ΔH_{hyd} for $Mg^{2+}(g)$ is larger than that for $Na^+(g)$ because $Mg^{2+}(g)$ attracts molecules of Water more strongly than $Na^+(g)$.
 - ΔH_{soln} = ΔH of a Solution reaction is the “dissolving” of something in a large excess of water. Solution involves first the breaking apart of all the species that are bonded to each other, and then there is an Hydration reaction. The reaction can be either endothermic or exothermic.
NB $\Delta H_{solution} = \Delta H_{lattice\ dissociation} + \Delta H_{hydration}$
 - ΔH_{solv} = ΔH of a Solvation reaction (the reaction between a solute and a solvent that is not water).
 - ΔH_{abe} = ΔH of Average Bond Enthalpy viz. the breaking of a particular type of bond (e.g. the C–H bond). The Average Bond Enthalpy is known by a number of other names such as Bond Dissociation Energy (ΔH_{bde})/Bond Enthalpy/Average Standard Bond Enthalpy/etc.
 - ΔH_{at} = ΔH of an Atomisation reaction (i.e. the forming of gaseous **atoms** of the substance from its standard state under standard conditions e.g. $Na(s) \rightarrow Na(g)$)

and many of the above will help us to look at this next one in detail

- ΔH_{latt} = **ΔH of Lattice Energy.** The **lattice dissociation enthalpy** is the enthalpy change needed to convert 1 mole of the substance (in its standard state and under standard conditions) into its scattered gaseous ions e.g. $MgCl_2(s) \rightarrow Mg^{2+}(g) + 2Cl^-(g)$. Lattice *dissociation* enthalpies are always positive. (For **lattice formation enthalpy**, reverse the sign.) **Although many metals have a lattice structure, the term “lattice” normally implies an ionic substance.**

Let me remind you of the definitions of some of the above.

¹ The word “number” is singular, therefore it is grammatically **incorrect** to say “there *are* a huge number of ΔH s”.

The calculation below is what we will be working towards

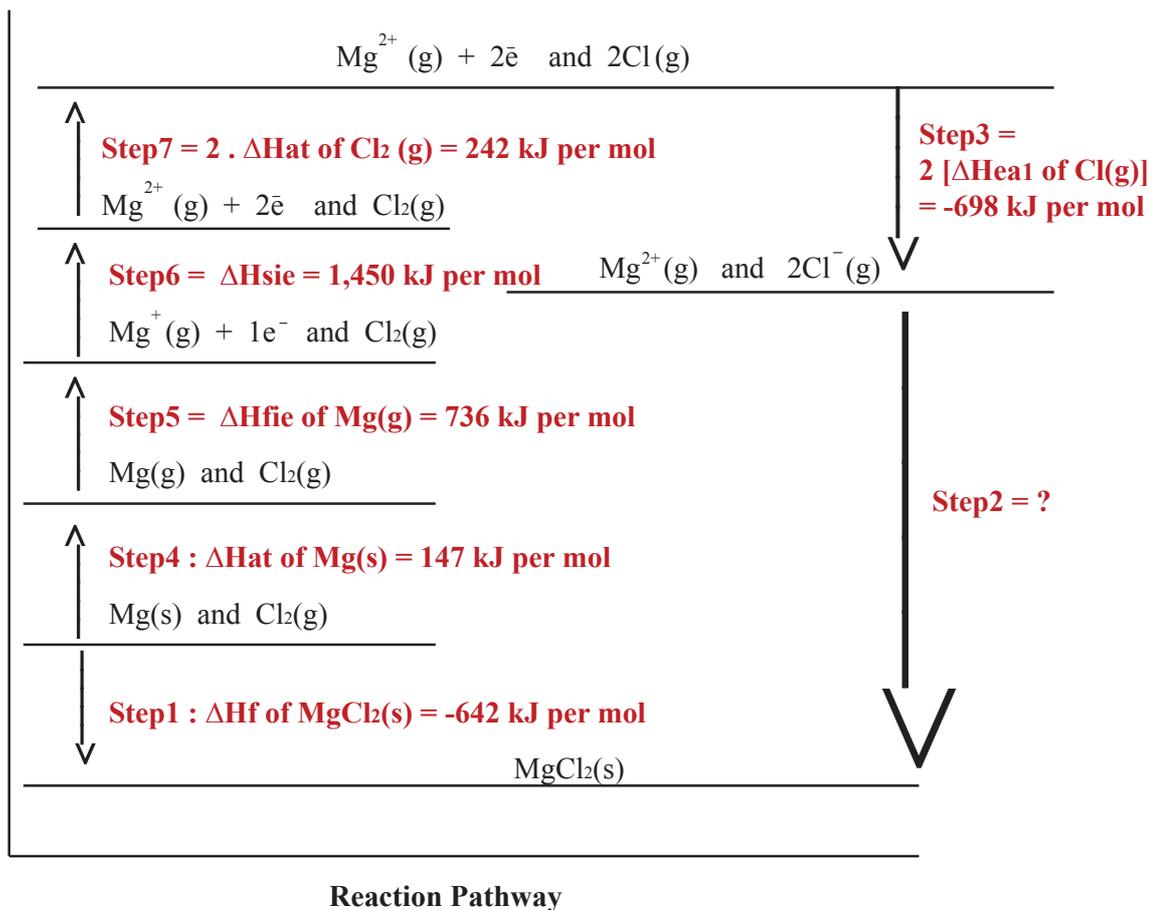
- Please remember that the distances between two parallel lines on an Enthalpy profile diagram **MUST** always be the same, therefore ignoring the signs (for the moment)

therefore $\text{Steps (1 + 4 + 5 + 6 + 7)} = \text{Steps (3 + 2)}$

$$\begin{aligned} \text{Step 2} &= \text{Steps (1 + 4 + 5 + 6 + 7)} - \text{Step 3} \\ &= (642 + 147 + 736 + 1,450 + 242) - (2 \times 349) \text{ kJ mol}^{-1} \\ &= 2,519 \text{ kJ mol}^{-1} \end{aligned}$$

NB I have NOT gone to the trouble of measuring all my vertical distances when drawing this next graph therefore the vertical distances are NOT proportionate to their values of ΔH (but in a perfectly drawn graph they would be).

Enthalpy (H)

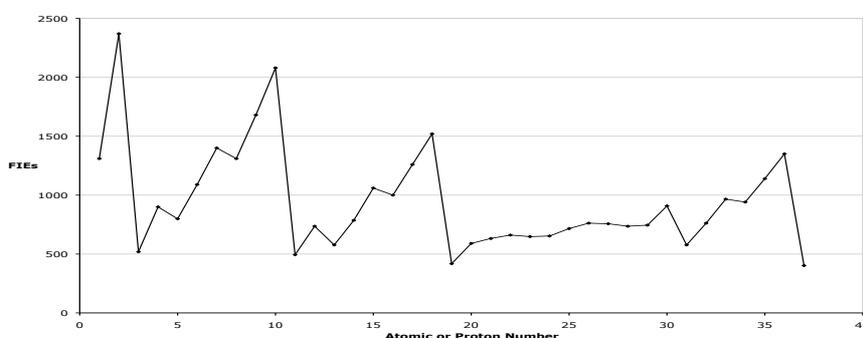


If you were to try to do the ΔH_{le} for $\text{Al}_2\text{O}_3(\text{s})$ you would find that there are a couple more steps in that one.

If you look at the diagram above, you will see that there many different ΔH s have been used, and **we need to know what is involved in every single one of them.**

A) ΔH of First Ionisation Energy, ΔH_{ie1}

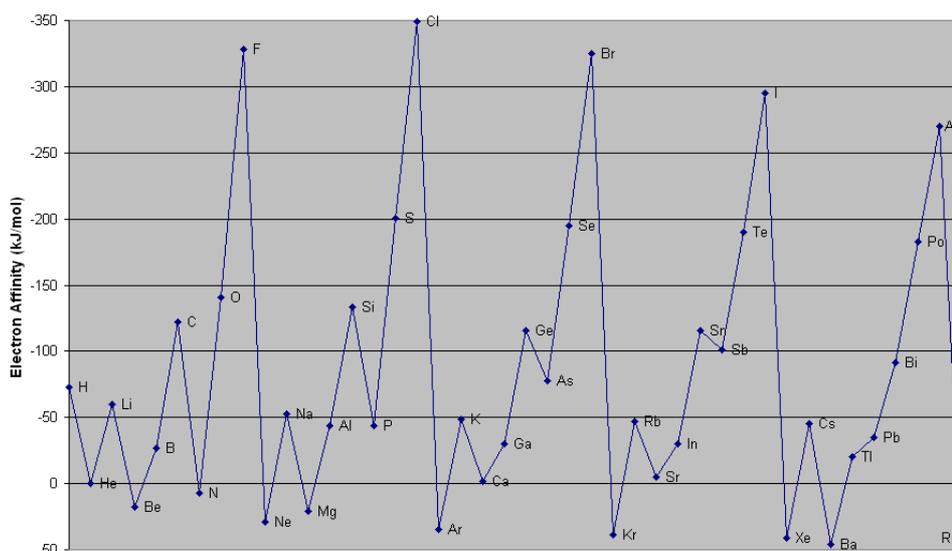
- The **Molar 1st Ionisation Energy** is the amount of energy that is required to remove one electron from every atom
 - in one mole of **ATOMS** of an element in its **GASEOUS state**, to give
 - one mole of **negatively charged electrons**, and
 - one mole of **GASEOUS IONS** each ion of which possesses a single positive charge
- Therefore, the ΔH_{ie1} = ΔH of First Ionisation Energy is **the amount of energy involved** when one mole of (for example) Hydrogen atoms in their gaseous form becomes one mole of Hydrogen ions each with a single positive charge in their gaseous form.
and this is represented by e.g. $\text{He (g)} - e^- \rightarrow \text{He}^+ \text{(g)}$; ΔH_{ie1} of Helium = $2,370 \text{ kJ mol}^{-1}$
and the ΔH_{ie2} would be given by $\text{He}^+ \text{(g)} - e^- \rightarrow \text{He}^{2+} \text{(g)}$; ΔH_{ie2} of Helium = $5,250 \text{ kJ mol}^{-1}$



B) ΔH of First Electron Affinity, ΔH_{ea1}

- The **Molar 1st Electron Affinity for an Element (or Molar 1st Electron Gain of an Element)** is the amount of energy released or required when
 - one electron is added to every atom in
 - one mole of **gaseous** atoms of an element to give
 - one mole of negatively charged **gaseous ions** of the element e.g.
 $\text{H(g)} + e^- \rightarrow \text{H}^-(\text{g})$ (Note the “**plus e^-** ” where there was a “**minus e^-** ” for the FIE.)
and ΔH_{ea1} of Hydrogen = $-77.7 \text{ kJ mol}^{-1}$.

Periodic Trends in Electron Affinity for the Main Group Elements



- I trust that you will have noticed that in most of the First Electron Affinities, energy is **released** when the first electron is added to a neutral gaseous atom of the element, and the largest amount of energy released is for the Halogens, while the Inert Gases (the Noble Gases) all have positive First Electron Affinities because they have already achieved the stability of an $ns^2 np^6$ electron configuration therefore they do not like to have any more electrons forced upon them.
- After that ALL (2nd/3rd/4th/5th/etc) Electron Affinities are **positive** because it then takes energy to force a negatively charged particle (an electron) onto a negatively charged electron cloud.

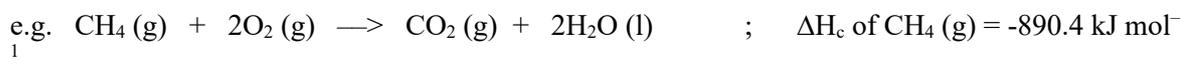
C) The Standard Enthalpy change of FORMATION, ΔH_f

- The Standard Enthalpy change of **FORMATION** is the net amount of energy involved when one mole of the substance under consideration is formed (under standard conditions²) **from its CONSTITUENT ELEMENTS** (I'll say that again, **ELEMENTS!**) when they are ALL are in their standard states.
- Please note that although this next reaction equation is *chemically* correct, it is **misleading thermodynamically**. **The ΔH_f of $SO_3(g)$ is NOT given by $SO_2(g) + \frac{1}{2} O_2(g) \rightarrow SO_3(g)$ THIS EQUATION IS WRONG FOR A ΔH OF **FORMATION** because SO_2 is NOT an **ELEMENT** (it is a **COMPOUND**)!**
- The correct statement is ΔH_f of $SO_3(g)$: $S(s) + \frac{3}{2} O_2(g) \rightarrow SO_3(g)$; $\Delta H = 395.7 \text{ kJ mol}^{-1}$ because Sulphur and Oxygen ARE the constituent **ELEMENTS** in their standard states and under standard conditions of the substance Sulphur Trioxide .
- Both the reaction equations above are chemically correct, but **only one of them expresses the ΔH_f of $SO_3(g)$.**

² Standard conditions = 1 atm of pressure / 298K / all concentrations at 1 mol dm⁻³, and all the substances have to be in their **Standard States** under these conditions. Please note that there is a variety of *alternative definitions* for the standard reference conditions of temperature and pressure. It is always important to know the reference temperature and reference pressure for the actual definition used.

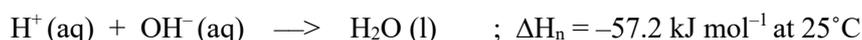
D) The Standard Enthalpy change of COMBUSTION, ΔH_c

- The Standard Enthalpy change of **COMBUSTION** is the net amount of energy involved (*in the case of the combustion of CH_4 gas, energy will be released*) when one mole of the substance under consideration in its standard state **is combusted completely in Oxygen** under standard conditions.



E) ΔH of a Neutralisation reaction, ΔH_n

- When we talk about “neutralisation” we tend to talk about the reaction between a strong acid and a strong alkali. We do so because the position of dynamic equilibrium of a weak acid/weak alkali will vary from weak acid to weak acid, and from weak alkali to weak alkali, therefore we can with certainty talk only about strong acids and strong alkalis neutralising each other.
- The ΔH of a Neutralisation reaction is thus the energy released (and when a strong acid and a strong alkali neutralise each other energy is always **released**) when a strong acid (e.g. HCl) and a strong alkali (KOH) react together to produce one mole of water viz.



- The ΔH_N for a strong acid and a strong alkali will always be in the range of 55-60 kJ mol^{-1} at 25°C because the reaction is between only **$H^+(aq) + OH^-(aq)$** and all the other cations and anions are just spectator ions and thus they do not participate in the reaction therefore altering the spectator ions will hardly affect the ΔH at all. (*In fact, the range is much narrower than 55-60 kJ mol^{-1} , and is probably more like 57-58 kJ mol^{-1} except for HF which has a $\Delta H_n = 69 \text{ kJ mol}^{-1}$ at 25°C).*)

Let me remind you of two ΔH s

- ΔH_{abe} = ΔH of Average Bond Enthalpy viz. **the breaking of a particular type of bond** (e.g. the C–H bond). The Average Bond Enthalpy is known by a number of other names such as Bond Dissociation Energy (ΔH_{bde})/Bond Enthalpy/Average Standard Bond Enthalpy/etc.
- ΔH_{at} = ΔH of an Atomisation reaction (i.e. **the forming of gaseous atoms of the substance** from its standard state under standard conditions e.g. $Na(s) \rightarrow Na(g)$).

ΔH_{abe} is about bond breaking, while

ΔH_{at} is about forming gaseous ATOMS of a substance.

F) ΔH of Atomisation, ΔH_{at} (conversion into single gaseous ATOMS of the substance), and a comparison with the ΔH of Average Bond Energy, ΔH_{abe} (the amount of energy required to break one mole of that particular BOND in its standard state under standard conditions). (I shall look at this in some detail.)

- The Standard Enthalpy change of **ATOMISATION** is the net amount of energy involved in the formation of one mole of **GASEOUS atoms** of the substance under consideration from its **standard state under standard conditions** whether that initial standard state be solid/liquid/or gas.
- Let us now look at the ΔH_{at} of some elements. I shall start by looking at those elements that are gases i.e. the standard state is “(g)” under standard conditions. Please therefore remember that

Hydrogen/Nitrogen/ Oxygen/and all the Halogens exist as diatomic molecules of gas as their standard state under standard conditions. However, not all substances exist as gases in their standard states. Nearly all metals are SOLIDS.

- The process is modestly simple when breaking apart say one molecule (i.e. two atoms) of Hydrogen viz.
 $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$. However, please remember that we always define ΔH in terms of one mole of the substance in which we are interested, and here we are interested in the amount of heat needed to break Hydrogen molecules into **one mole of Hydrogen atoms**, therefore ΔH_{at} of $\text{H}(\text{g})$ is the amount of energy involved in



- The ΔH for the breaking of (for example) the H–H bond is **NOT the same as the ΔH of Atomisation** and bond breaking is called by a confusing number of different names such as Average Bond Enthalpy/Bond Dissociation Energy/Bond Enthalpy/Average Standard Bond Enthalpy/Bond Energy Term/etc, (and I shall talk about this ΔH in Section “G”). However, “**Average Bond Enthalpy**” (abe) is probably as good a name as any – and all of these different names represent **the amount of energy required to break one mole of that particular BOND in its standard state under standard conditions**.
- The value of the ΔH_{abe} for the H–H bond is $436.0 \text{ kJ mol}^{-1}$, and this is exactly twice as much as the ΔH_{at} of $\text{H}(\text{g})$ which = $218.0 \text{ kJ mol}^{-1}$. **This is not in the least surprising because when you break one mole of H–H bonds you get TWICE as many H atoms as you need when you are considering the ΔH_{at} of $\text{H}(\text{g})$.** The same logic would apply to Oxygen where the ΔH_{at} of $\text{O}(\text{g})$ is 248 kJ mol^{-1} and the ΔH_{abe} of the O–O bond is 498 kJ mol^{-1} (and for Nitrogen it is 473 vs 944 kJ mol^{-1}).

- The strong bonds between the atoms in a molecule are called **INTER**-molecular bonds (in contrast to the weak forces of attraction between molecules that are called **INTRA**-molecular van der Waals’ forces of attraction or London Dispersion forces or Debye forces). The amounts of energy required to break different bonds depends on whether they are single/double/or triple bonds, and for the gases in Period 2

kJ mol^{-1}	Nitrogen(g) ($\text{N}\equiv\text{N}$ bond)	Oxygen(g) ($\text{O}=\text{O}$ bond)	Fluorine($\text{F}-\text{F}$ bond)
ΔH_{at}	473	248	79.08
ΔH_{abe}	944	498	159.0

- That is all nice and simple, and you will notice that this relationship between ΔH_{at} and ΔH_{abe} holds good for Fluorine and Chlorine – but **it does not do so for Bromine and it does not do so for Iodine**. For the early Halogens in Group VII

kJ mol^{-1}	Fluorine(g)	Chlorine(g)	Bromine(l)	Iodine(s)
ΔH_{at}	79.08	121.8	111.7	106.7
ΔH_{abe}	159.0	243.0	193.0	151.0

- You may at first be surprised by this until you remember that the standard state of Fluorine and Bromine is that of a **gas**, but the standard state for Bromine is a **LIQUID**, and the standard state for Iodine is a **SOLID**. The breaking of a Br–Br bond will therefore need energy first to overcome the vdW/London/Debye forces of attraction between the molecules of $\text{Br}_2(\text{l})$, and convert them into gaseous molecules of $\text{Br}_2(\text{g})$, and then only will the Br–Br bonds get broken.
- The vdW/London/Debye³ **INTRA**-molecular forces of attraction are broken first, and then the **INTER**-molecular forces of attraction get broken. However, vdW/London/Debye forces are not very strong, and the length of the Br–Br bond is much greater than the length of an F–F bond or

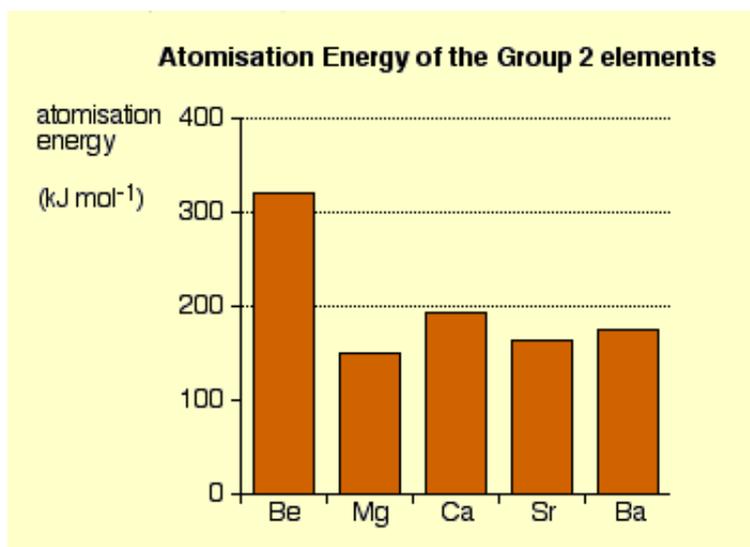
³ There is some disagreement as to whether they should be call after Johannes van der Waals or Fritz London or Peter Debye (who all got Nobel Prizes for their contributions). Let us not concern ourselves with that dispute here.

the length of a Cl–Cl bond – and the amount of energy needed to break a long bond is less than the amount of energy needed to break a short bond.

NB When you are considering Iodine, you will then need to remember that Iodine does not melt from a solid to a liquid and then boil from a liquid to a gas. **Iodine sublimates straight from a solid to a liquid.**

- OK, let us now look at the ΔH of solids.
- I believe that an understanding of the differences in the ΔH of metals is not part of any of the UK Exam Boards' Syllabuses, and the reason for this is that deep divisions exist with regard to the explanations given. If you go to <https://www.chemguide.co.uk/inorganic/group2/properties.html> (almost to the bottom of the page) you will find the very complicated discussion to which I refer. All that I intend to do is to give you here are some numbers and then I will move on to Average Bond Enthalpies or Bond Dissociation Energies (because the science involved is too complex for 'A' Level candidates). Here are the numbers

e.g. $\text{Na (s)} \rightarrow \text{Na (g)}$; ΔH_{at} of Na (g) = 107.0 kJ mol⁻¹.
and $\text{Mg (s)} \rightarrow \text{Mg (g)}$; ΔH_{at} of Mg (s) = 146.0 kJ mol⁻¹.
and $\text{Al (s)} \rightarrow \text{Al (g)}$; ΔH_{at} of Al (s) = 314.0 kJ mol⁻¹.



Source: <https://www.chemguide.co.uk/inorganic/group2/properties.html>

G) ΔH of Average Bond Enthalpy or Bond Dissociation Energy, ΔH_{abc} or ΔH_{bde}

- I have written about Average Bond Enthalpy/or Average Standard Bond Enthalpy/or Bond Energy Terms, and this is what I have said

Average Bond Enthalpy or Bond Dissociation energy or Bond Energy Term

- These three phrases refer to exactly the same thing viz. **“the average amount of energy that is required to break one mole of a particular type of covalent bond in differing situations”**. [Let me repeat that last bit **“Covalent bond”** and NOT **“Ionic bond”**.] **NB To break a bond requires energy.**

For instance, the Average Bond Enthalpy or Bond Dissociation energy or Bond Energy Term for

Breaking the following bonds is Average Bond Enthalpy (kJ mol⁻¹)

(Endothermic processes therefore “+ve” figures)

(Approximately)

• O–O	146	
• O=O	496	
• H–H	436	
• C–H	412	
• C–C	347	
• C=C (C double bond C)	612	
• C triple bond C	837	

- Any good data book (e.g. “*Chemistry Data Book*” Stark & Wallace, ISBN 0-7195-3951-X) will contain these numbers – and any numbers that you need in the exam will be provided for you in the exam.
- I do however want you to appreciate one important thing i.e. *there is no such thing as a PRECISE figure for an Average Bond Enthalpy/Bond Dissociation Energy* – and the explanation for this is as follows.
- Let me start by asking you a question. “*Would it take exactly the same amount of energy to break each C–H bond in CH₄ (g)?*”, and if your answer is “*No!*”, then you are absolutely spot on! After breaking the first C–H bond in CH₄ (g), the central C atom is now attached to only three H atoms – and it will therefore take a (slightly) different amount of energy to break the next C–H bond; and, when we go to break the next C–H bond after that one, the central C atom is holding on to only two H atoms, therefore the circumstances have changed again – therefore the amount of energy required to break the third C–H bond is again different, and so on!
- In fact, the amount of energy required to break each of the successive C–H bonds has been found, by experimentation, to be

Reaction	ΔH (kJ mol⁻¹)
• CH ₄ (g) → CH ₃ (g) + H (g)	435
• CH ₃ (g) → CH ₂ (g) + H (g)	444
• CH ₂ (g) → CH (g) + H (g)	440
• CH (g) → C (g) + H (g)	<u>343</u>
Bond Energy Term = Average =	<u>415.5 kJ mol⁻¹</u>

and if you add up and average the four different figures above, then you will get 415.5 kJ mol⁻¹, and you will see that this figure is not very different from the Average Bond Enthalpy/Bond Energy Term for **ALL** C–H bonds in all the molecules in which they may occur (viz. 412 kJ mol⁻¹ as shown in the first table above)! However, if we did the same exercise for C₂H₆ the answer would be different, and different again for C₃H₈. *There is no precise answer for ΔH for a C–H bond. It all depends on the circumstances in which you are breaking (or forming) the bond.*

- There is a HUGE number of possible C–H bonds in a HUGE number of different Carbon molecules, and you can see now that there is no one single precise figure for *Average Bond Enthalpies!* Bond Enthalpies are merely the average figure for breaking one mole of a given bond in all the differing molecules in which that bond can be found (and if you are a Mathematician, then you will be aware that there are many different ways of “averaging” a set of numbers e.g. a simple arithmetic average/a weighted arithmetic average/a geometric average/an exponential average/ ... and so on).

- If I were referring to the breaking of the first bond in CH₄ (g) then I would specify

$$\text{CH}_4(\text{g}) \longrightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g}) \quad ; \quad \Delta H_{\text{abc}} = 435 \text{ kJ mol}^{-1}$$

but if I were referring to the breaking of a C–H bond in general then I would specify

$$\Delta H_{\text{abc}} \text{ of C–H} = 415.5 \text{ kJ mol}^{-1}$$

H) ΔH of Solvation, ΔH_{solv}

- This refers to the ΔH involved when one mole of a substance in its standard state under standard conditions dissolves in a large excess of a specified solvent **other than Water** (for which we have $\Delta H_{\text{Solution}}$).

I) ΔH of Solution, ΔH_{soln}

- This refers to the ΔH involved when one mole of a substance in its standard state under standard conditions dissolves in a large excess of **water**⁴. The water ‘breaks apart’ the substance, and water molecules will then surround and react with the individual ions in the substance. The ΔH of Solution will thus involve the ΔH of Hydration (next one down) viz. $\Delta H_{\text{solution}} = \Delta H_{\text{lattice dissociation}} + \Delta H_{\text{hydration}}$
- “Like dissolves like” and since Water is a polar substance (Water molecules have a partial separation of charge in them), then Water will (in general) dissolve only polar substances. Therefore the solute in the ΔH of Solution will be an **ionic substance**. When something “dissolves” in water, the water molecules rush up to the substance and grab one ion (at a time) off the substance until all the ions have been pulled apart and surrounded by water molecules.
- Solubility is influenced by a number of factors. First of all you need to know the ΔH of Lattice Enthalpy (i.e. the amount of energy required to break apart one mole of the giant ionic lattice crystal structure that is to be dissolved *into its gaseous ionic constituents*), and then you need to know the ΔH of Hydration of each ion involved (i.e. the amount of energy given off when one mole of every one of the broken off ions becomes surrounded by molecules of water), and this is determined by the temperature of the solvent /the charge density of the metal cation/etc.

J) ΔH of Hydration

(ΔH_{hyd} is the amount of energy involved when one mole of gaseous ions of an element reacts with an excess of water molecules)

- This refers to the situation where every ion in an ionic substance becomes surrounded by water molecules e.g.

$$\text{Cl}^-(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Cl}^-(\text{aq}).$$
- The energy involved is that of the formation of bonds between the water molecules and the ions. Hydration enthalpies are always negative (because when bonds are formed energy is **released**, and when bonds are broken energy is **required**). The *size* of/the value of the hydration enthalpy will be influenced by the charge density of the metal cation involved.

⁴ Textbooks refer to “an infinitely dilute solution”, but this is rubbish (I shall not use the more impolite word) because if there is a given amount of water then there is no possibility of the concept of infinity entering into the situation.

And now at last we have come to the ΔH on which I wanted to spend some time because it comes up in the exams again and again. (The one on the next page from AQA in June 2015 is just one of many Born-Haber cycles or Enthalpy Profile diagrams that have come up in the last half century!)

2

Section A

Answer all questions in the spaces provided.

1 (a) Define the term **electron affinity** for chlorine. [2 marks]

The enthalpy change for the formation of one mole of chloride ions from chlorine atoms in their gaseous states.

1 (b) Complete this Born-Haber cycle for magnesium chloride by giving the missing species on the dotted lines. Include state symbols where appropriate. The energy levels are not drawn to scale. [6 marks]

MgCl₂(s)

NB You can get different answers from different data books for ΔH_{le} e.g. the figures I have used on page 12 gives an answer of $2,519 \text{ kJ mol}^{-1}$ for MgCl_2 .

K) ΔH of Lattice Energy, ΔH_{le}

- You may have noticed that I have taken you through a large number of ΔH s before attempting to explain **ΔH of Lattice Energy, ΔH_{le}** , and this I have done deliberately because there quite a few separate steps involved in ΔH of Lattice Energy, ΔH_{le} . **In the one that I am going to do over the next few pages i.e. that for MgCl_2 , there are seven steps involved.**
- I am now going to take you through the steps for a modestly complicated ionic substance MgCl_2 because in the olden days that was the basis of an exam question very often (because it brings together all the stuff that you need to know about ΔH s) and because (since 2015) they have started asking more difficult questions in the Organic exam paper.

The Lattice enthalpy of MgCl₂

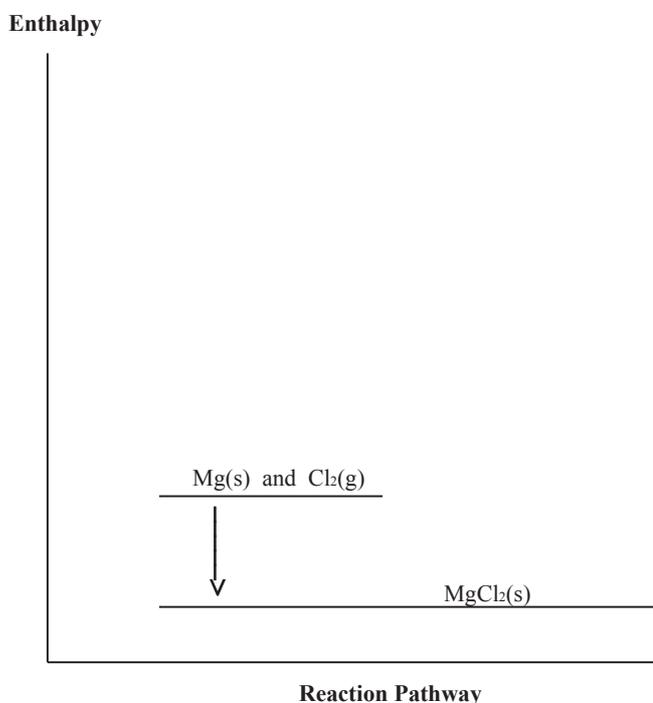
NB Please could you remember that in all the transitions that follow we are going to calculate the **Lattice Enthalpy of MgCl₂**, therefore we need to keep track of the values of all the ΔH s involved and then at the end do a calculation that will bring all of them together to obtain the ΔH_{le} of MgCl₂.

I am going to take you through every step in the calculation, therefore it will be repetitive – but I would rather give you a solid grounding in the subject than (perhaps wrongly) assume that you know what I am talking about.

I am going to make the mathematics of the calculations a tiny bit easier by giving all the ΔH s values in whole numbers. (*I am not going to use any decimal points.*)

Step 1, the ΔH of Formation of MgCl₂(s) = 642 kJ mol⁻¹

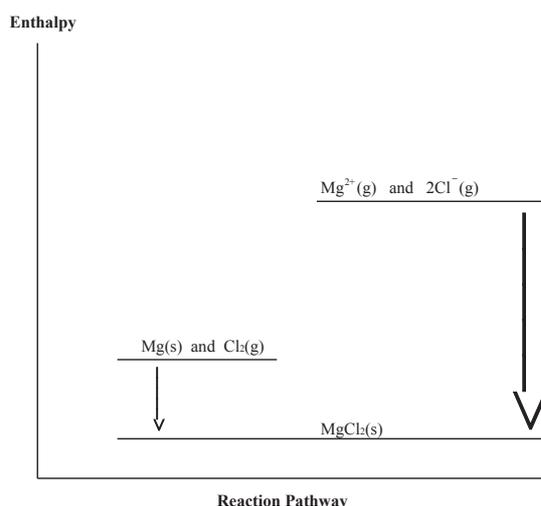
- We want to finish up with the ionic substance MgCl₂, therefore let us start by **forming** MgCl₂. For the ΔH of Formation of MgCl₂ we need to start with the **constituent elements** of MgCl₂ **in their standard states and in their standard conditions** (and we will need to look up the ΔH_f for ONE MOLE of MgCl₂).
 ΔH_f of MgCl₂ (s) is given by the equation $\text{Mg(s)} + \text{Cl}_2(\text{g}) \longrightarrow \text{MgCl}_2(\text{s})$
- I can therefore draw this first step as part of a Born-Haber cycle/an Enthalpy Profile diagram viz.



Step 2, the ΔH of Lattice Enthalpy of $\text{MgCl}_2(\text{s}) = ?$ (and the data books show it as $-2,495 \text{ kJ mol}^{-1}$)

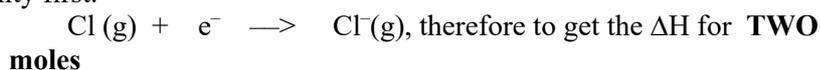
- For the Molar Lattice Enthalpy of formation of MgCl_2 we will need to bring together one mole of the positively charged gaseous **IONS**⁵ of Mg (i.e. $\text{Mg}^{2+}(\text{g})$) and **TWO** moles of the negatively charged gaseous **IONS** of Chlorine (i.e. $2\text{Cl}^{-}(\text{g})$), so let us do that viz.

ΔH of Lattice Enthalpy of $\text{MgCl}_2(\text{s})$ is given by the equation $\text{Mg}^{2+}(\text{g}) + 2\text{Cl}^{-}(\text{g}) \rightarrow \text{MgCl}_2(\text{s})$



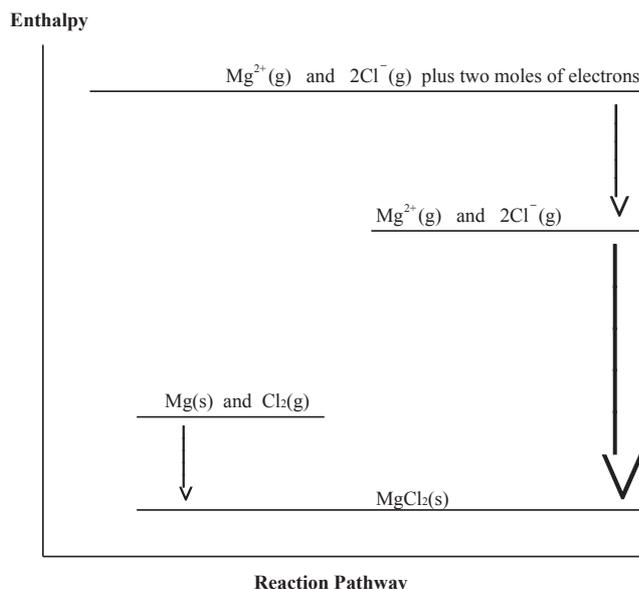
Step 3, the ΔH of the First Electron Affinity of Chlorine (g) = -349 kJ mol^{-1}

- OK, now let us think about how we got to $\text{Mg}^{2+}(\text{g})$ and $2\text{Cl}^{-}(\text{g})$. Well, a few moments of thought will remind us that we need to think about Ionisation Energy (to get positively charged metal Magnesium ions) and Electron Affinities (to get negatively charged non-metal Chloride ions). Let us do the Electron Affinity first.



but please remember that here we need two moles of Chloride ions to get $\text{MgCl}_2(\text{s})$ forming, therefore the amount of energy that will be involved is $(-349 \times 2 = -698) \text{ kJ mol}^{-1}$.

⁵ Metal atoms give up/transfer electrons to non-metal atoms when an ionic substance is formed.



- Yes, but how did we get the gaseous Chloride ions and the two moles of electrons?
- The answer to that question is that when we took two electrons off each atom of Magnesium to get the First and Second Ionisation Energies of Magnesium respectively (736 and $1,450 \text{ kJ mol}^{-1}$) that supplied us with two electrons, and that allowed us to place those two electrons on the two gaseous Chlorine atoms.

Therefore

Step 4, the First Ionisation Energy of Magnesium (s) = 736 kJ mol^{-1}

ΔH_{ie1} of Mg(g) is given by the equation $\text{Mg(g)} - e^{-1} \longrightarrow \text{Mg}^{+}(\text{g})$
and

Step 5, the Second Ionisation Energy of Magnesium (s) = $1,450 \text{ kJ mol}^{-1}$

ΔH_{ie2} of Mg(g) is given by the equation $\text{Mg}^{+}(\text{g}) - e^{-1} \longrightarrow \text{Mg}^{2+}(\text{g})$

- but, that then brings us to the question “but how did we get Mg(g) in the first place, and for that matter, how did we get Cl(g) ?”

Step 6, the ΔH of Sublimation or Atomisation⁶ of Magnesium (s) = 147 kJ mol^{-1}

ΔH_{at} of Mg(s) is given by the equation $\text{Mg(s)} \longrightarrow \text{Mg(g)}$

and for Chlorine

Step 7, the ΔH of Atomisation of Chlorine (g) = 121 kJ mol^{-1}

ΔH_{at} of $\frac{1}{2} \text{Cl}_2(\text{g})$ is given by the equation $\frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{Cl(g)}$, but please remember that here we need two moles of Cl(g) , therefore there will be twice as much energy involved ($=242 \text{ kJ mol}^{-1}$).

- OK, we are now in a position to put everything together and solve for the missing value.

⁶ The two are identical for Magnesium.

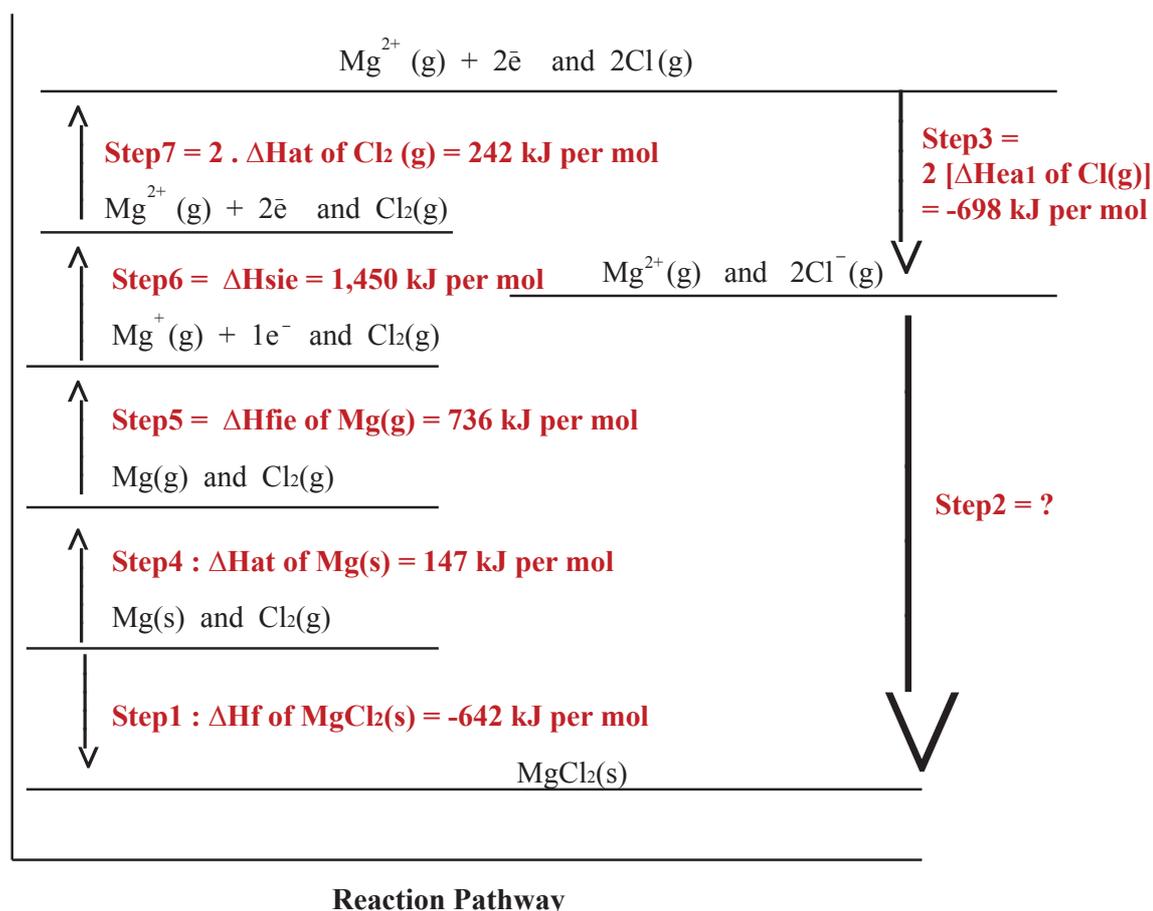
- Please remember that the distances between two parallel lines on an Enthalpy profile diagram MUST always be the same, therefore in the Born-Haber cycle/Enthalpy Profile diagram overleaf (ignoring the signs for the moment)

therefore $\text{Steps (1 + 4 + 5 + 6 + 7)} = \text{Steps (3 + 2)}$

$$\begin{aligned} \text{Step 2} &= \text{Steps (1 + 4 + 5 + 6 + 7)} - \text{Step 3} \\ &= (642 + 147 + 736 + 1,450 + 242) - (2 \times 349) \text{ kJ mol}^{-1} \\ &= 2,519 \text{ kJ mol}^{-1} \end{aligned}$$

Please note that I have NOT gone to the trouble of measuring all my vertical distances when drawing this next graph therefore the vertical distances are NOT proportionate to their values of ΔH .

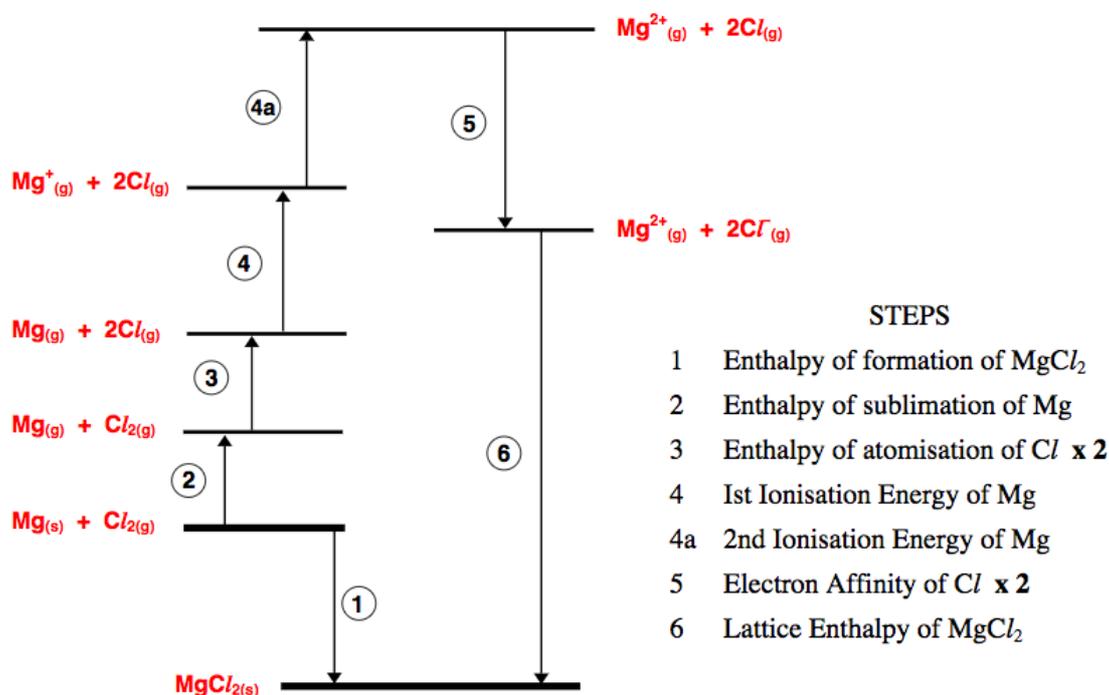
Enthalpy (H)



- Exactly the same calculation could have been performed using a Hess-cycle, but it is easier to use Enthalpy Profile diagrams/Born-Haber cycles to do the calculations for Lattice Enthalpies (because the same vertical distance always involves the same ΔH i.e. the same difference in Enthalpy).

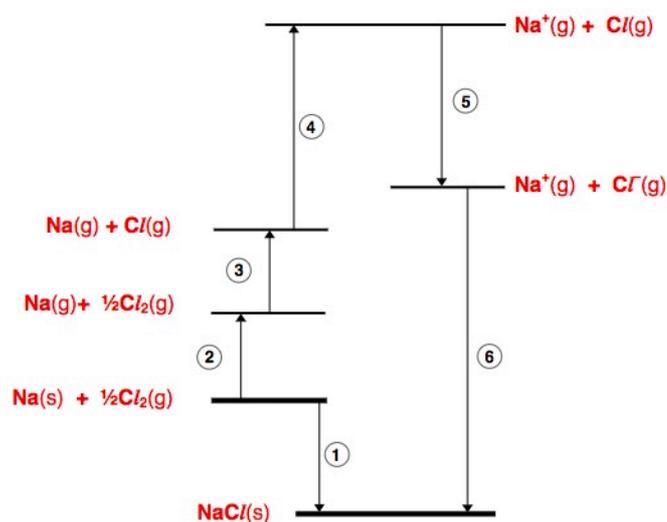
- Knockhardy gives the same Enthalpy Profile Diagram/Born-Haber cycle as

BORN-HABER CYCLE FOR MAGNESIUM CHLORIDE

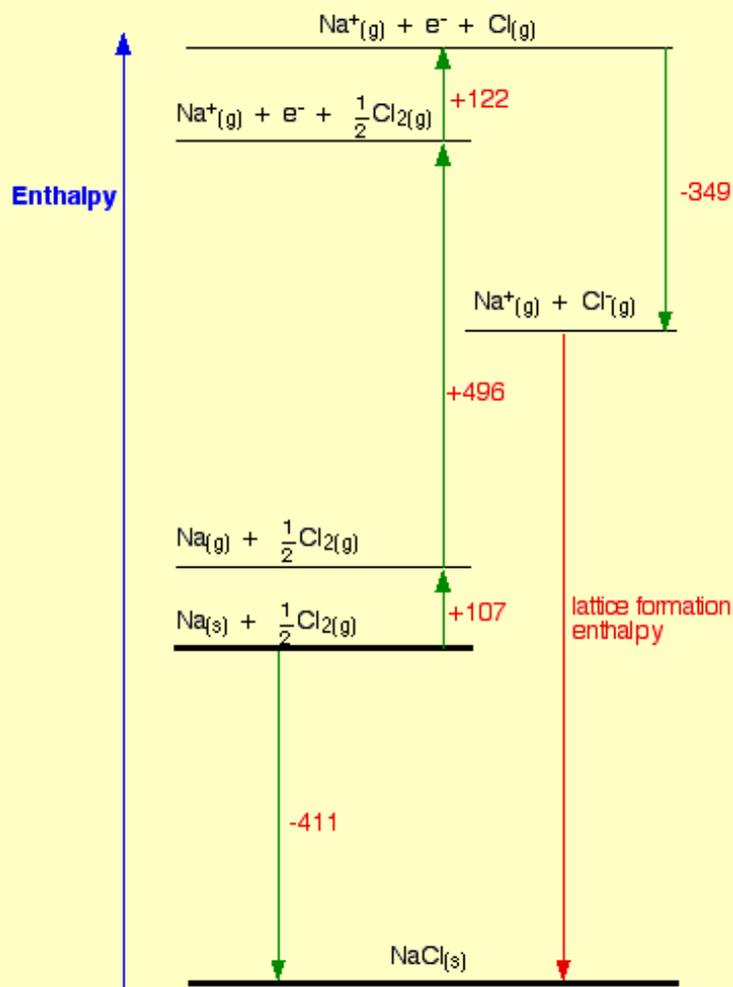


- Now, would **you** like to try to calculate the ΔH_{lc} for Sodium Chloride?

BORN-HABER CYCLE FOR SODIUM CHLORIDE



- Use your search engine to look up all the different ΔH s, and the answer you should get is shown overleaf



$$-411 = +107 + 496 + 122 - 349 + \text{LE}$$

$$\text{LE} = -411 - 107 - 496 - 122 + 349$$

$$\text{LE} = -787 \text{ kJ mol}^{-1}$$