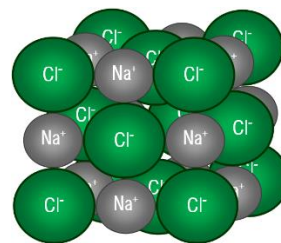


Lattice Enthalpy and Born-Haber Cycles



Introduction

I am not normally keen to begin any lesson with a definition. However, in this case, I will make an exception.

I will begin by presenting you with the definition of **Lattice Enthalpy**, $\Delta_{LE}H$.

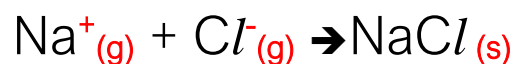
Lattice Enthalpy, $\Delta_{LE}H$

This is the enthalpy change when 1 mole of ionic lattice is formed from its constituent gaseous ions (strictly, when the gaseous ions approach from infinite separation!)

Note that the subscript (in this case **LE**), should be placed **before the symbol**, H. You will often find this subscript placed after the H. IUPAC* states that that the subscript should be placed before H. To place it after the H would suggest that there is a change in the value of the named enthalpy change. This clearly not the case so we place it before H.

The simplest and most common example of the is probably the **Lattice Enthalpy** of sodium chloride $\Delta_{LE}H$ (NaCl).

This definition is represented by the chemical equation:



I am now going to ask you to accept that this rather strange enthalpy change was a fundamental jigsaw piece in the understanding of chemical bonding. This contribution will become obvious, later.

If there was ever an example that reinforces the importance of Hess's Law, it is Lattice Enthalpy. If you look at the full definition of Lattice Enthalpy (including the bit about 'approaching from infinite distance'), you should surely realise that this is impossible to achieve, practically. Even if you were able to have a bag containing a mole of gaseous cations and one bag of gaseous anions, getting infinitely far from the lab (in opposite directions) to release them is somewhat problematic! Without Hess's Law, it would be impossible to find the value for this process (I have asked you to accept that we really do need this value).

At this stage, the a physicist may say that the energy released when 1 mole of lattice from its constituent gaseous ions must simply be the reverse of the energy required to overcome the forces of attraction within the ionic lattice. This is true. There is a law in physics, Coulomb's Law, which can allow us to calculate the force of attraction or repulsion between 2 charges if you know the size of the charge and their separation.

$$\text{Force} = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2}$$

Coulomb's law

The charges on ions (Q_1 and Q_2) are known and the distance between ions (r) can be found by X-Ray crystallography. Clearly, it is complicated by the fact that there is one mole of anions and one mole of cations in NaCl. There are attractions between anions and cations but repulsions between the anions and between the cations. The arrangement of the ions within the crystal has an influence. If you are interested in how this is treated, you could look up the '**Born-Landé**' equation which accounts for all these factors. This is quite complicated, but **it is possible** to use the principles of physics to determine the energy released when a mole of ionic lattice is made from the constituent gaseous ions.

*IUPAC stands for the *International Union of Pure and Applied Chemistry*. This organisation is responsible for developing the many rules and conventions that we use in chemistry.

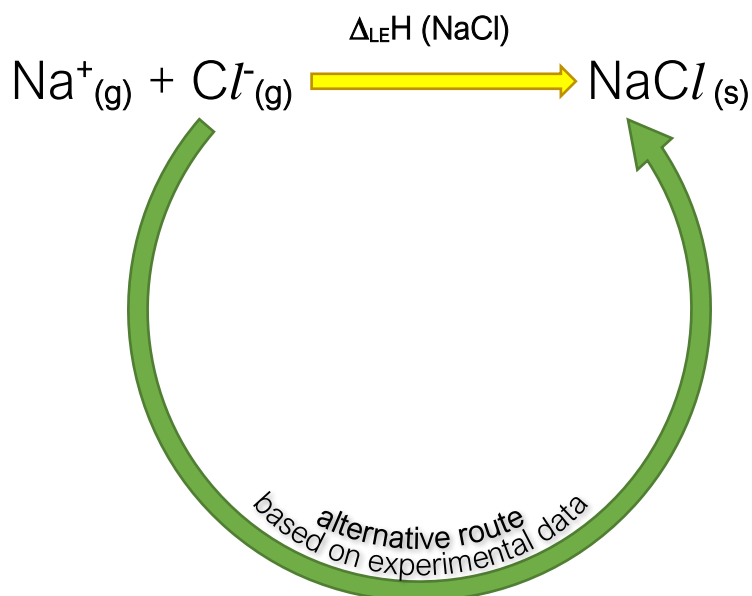
This theoretical value is based on the assumption that the ions are 'point charges' This is how we have always thought of ions; as simple, perfectly spherical, charged particles.

The *theoretical value* for $\Delta_{LE}H(\text{NaCl}) = -766 \text{ kJ mol}^{-1}$

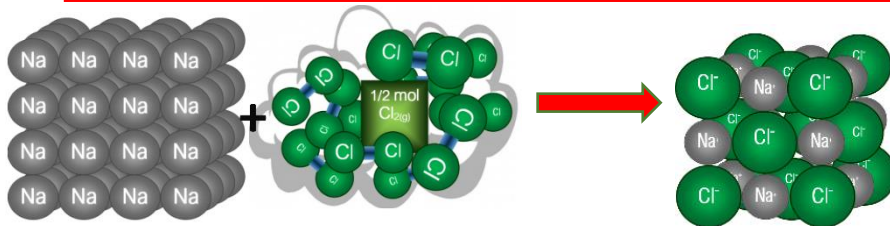
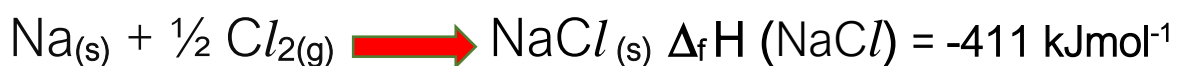
Chemists generally like to solve problems practically. It would be a shame if the chemist couldn't approach this problem of Lattice Enthalpy with a **Hess Cycle** based on **experimentally determined enthalpy changes!**

Let's try to build up an **alternative route** that can connect **the gaseous anions and cations** with the **ionic lattice**.

In the diagram below, we are going to think about enthalpy changes that can be put together to give us the **GREEN ROUTE**



The first enthalpy change that could fill part of the green route is an enthalpy change that you are familiar with; the **enthalpy of formation** of sodium chloride. $\Delta_f H(\text{NaCl})$.



enthalpy of formation, $\Delta_f H$

'This is the enthalpy change that accompanies the formation of 1 mol of a compound in its standard state from its elements in their standard states, under standard conditions'

You should already know this definition. If you don't, you must get it committed to memory!

I would imagine that you could predict that this is an exothermic enthalpy change if you simply consider the very highly reactive nature of the elements, sodium and chlorine. Sodium 'burns' very brightly in chlorine gas!

I'm going to start building a Hess Cycle. However, unlike the ones you may have seen in Year 12, this cycle will be a little bit stricter in its layout (which makes it easier to understand!)

The only arrows that we will draw will be straight up or down.

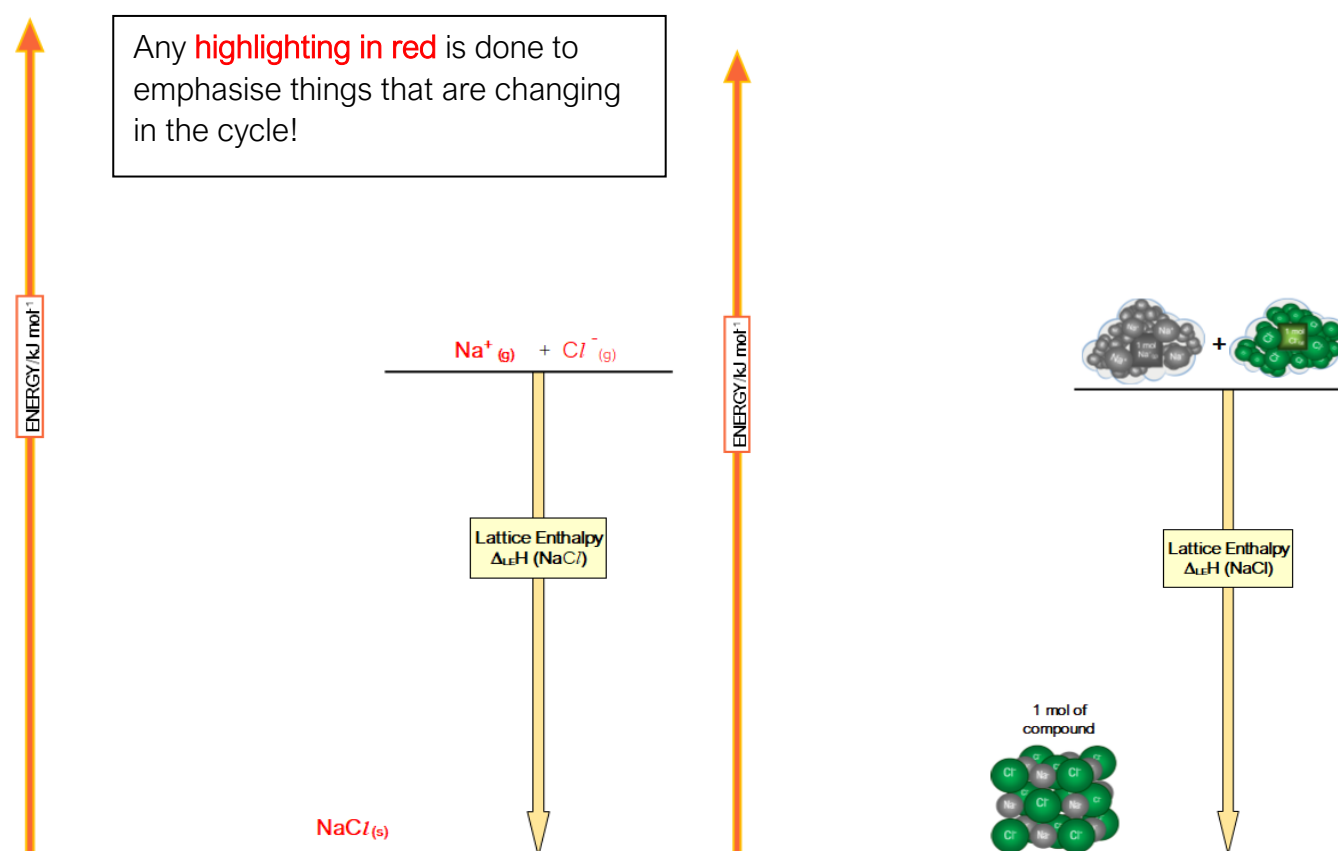
↑ UP will represent **endothermic changes** and

↓ DOWN will represent **exothermic changes**.

Also, it is typical for the length of the arrow to represent the magnitude of the enthalpy change. For example, a very **long downward arrow** will represent a **highly exothermic process**.

Over the next few pages, we will construct one of these cycles. They were developed based on the work of Max Born and Fritz Haber (and Landé) so they are called **Born-Haber Cycles**.

The first diagram represents what we are trying to find out, $\Delta_{LE}H(\text{NaCl})$. **Lattice enthalpies must always be exothermic** as strong ionic bonds are being made. On the right is a cartoon version to help illustrate the processes.



For each additional enthalpy change, I will represent the cycle with both formulae and cartoons. The pictures help you to visualise what's happening.

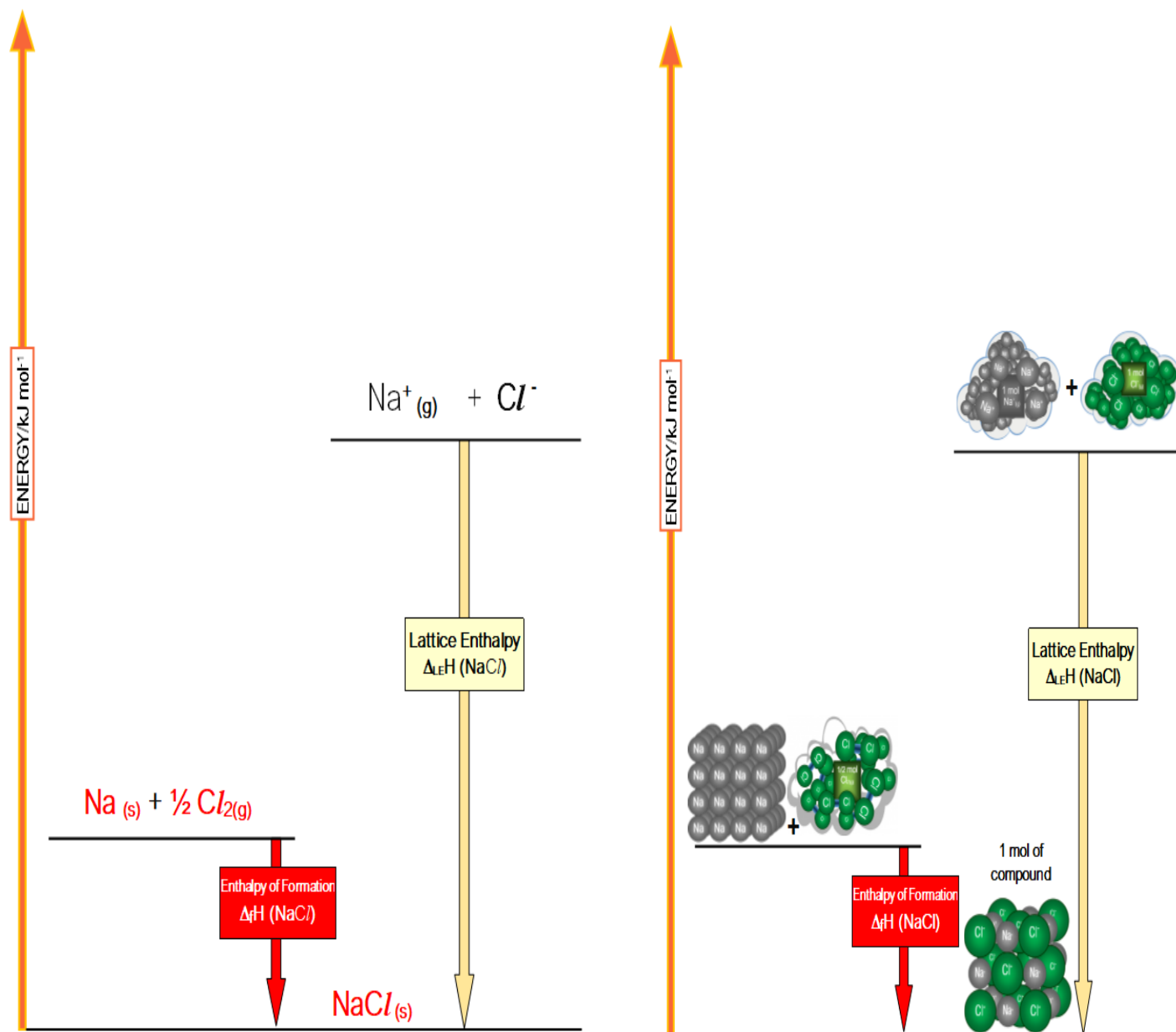
******IMPORTANT NOTE! READ!******

You will often see slightly **different values for the same enthalpy change**, depending upon your source! When you use data from different sources, it leads to slight differences in calculated values. Don't worry about a few kJ mol^{-1} difference over many hundreds or thousands of kJ mol^{-1} .

When selecting data over 25 years, I have tried to make them all agree with each other, but it is simply impossible. So, don't panic if you see different literature values to these presented here.

In an exam question, all the data will be internally consistent.

We have a 2nd enthalpy change that we can add to our growing Born-Haber Cycle. This is simply the enthalpy of formation of sodium chloride, $\Delta_f H(\text{NaCl})$.



We now need to convert the sodium from a shiny metallic solid **element** into **gaseous sodium ions**. And then convert chlorine from a diatomic **element** to **gaseous chloride ions**.

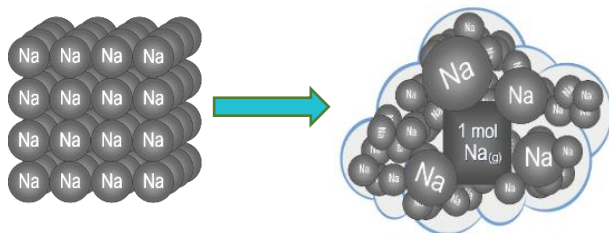
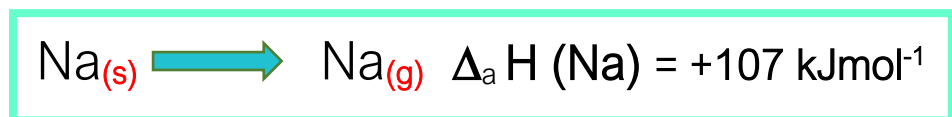
The way to tackle this is to concentrate on sodium first and then turn our attention to chlorine!

Crystalline **elemental sodium** needs to become **gaseous atoms** before the sodium can be ionised.

This change is known as **atomisation** and has a named enthalpy change associated with it.

This is shown on the next page.

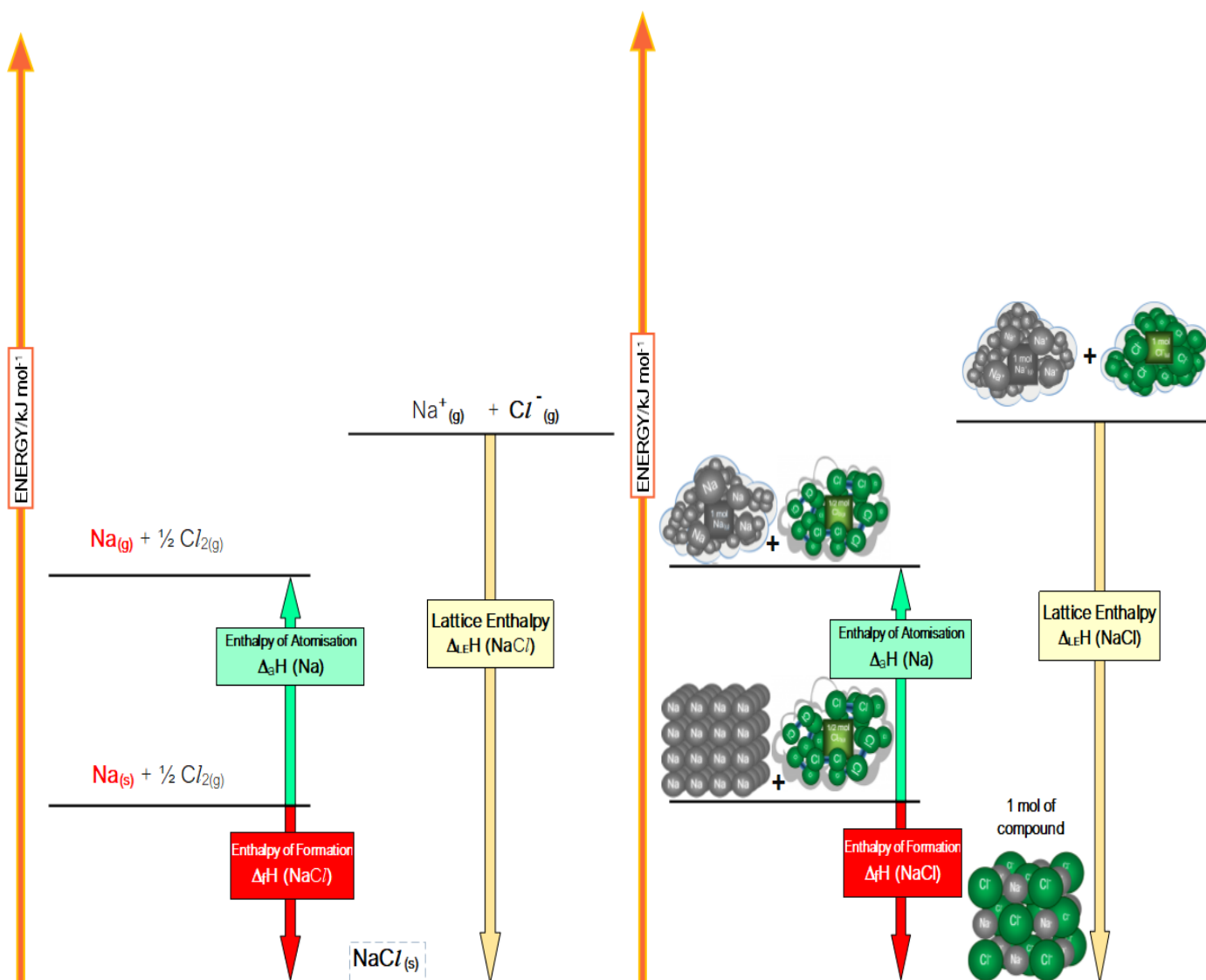
The enthalpy change for this process is the **enthalpy of atomisation**. $\Delta_a H (\text{Na})$



enthalpy of atomisation, $\Delta_a H (\text{Na})$

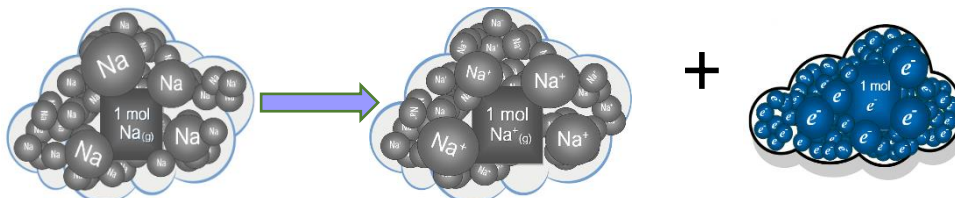
'This is the enthalpy change that accompanies the formation of **1 mol of gaseous atoms** from the element in its standard state'.

We need to make **1 mol of sodium atoms** so we need to 1 mole of sodium metal. You must remember that this enthalpy change is all about **1 mole of atoms made**. There is a quiz on enthalpy change definitions!



Gaseous sodium atoms now need to be converted into gaseous sodium ions.

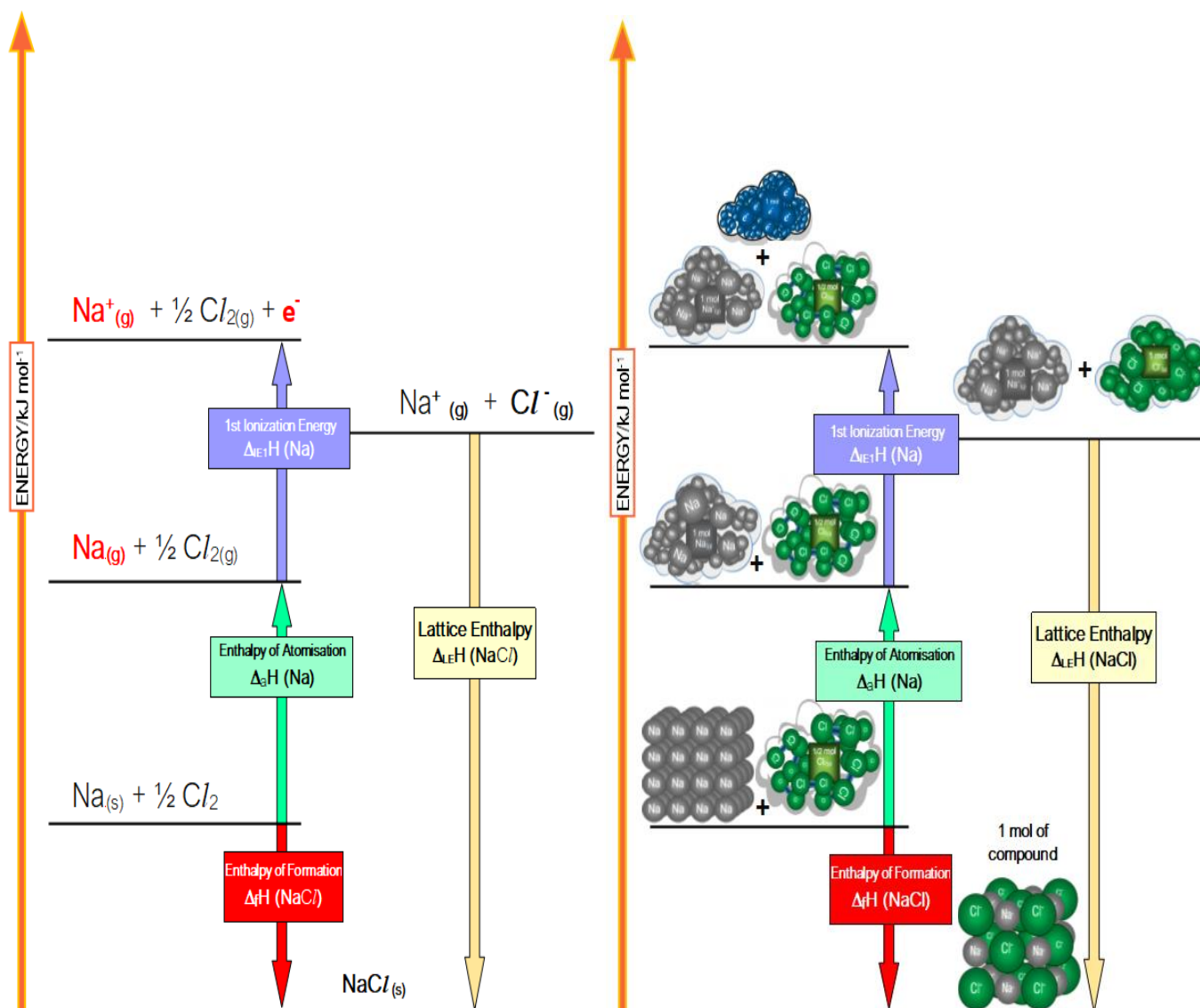
The enthalpy change for this process is the 1st Ionisation Energy, $\Delta_{\text{IE}1} \text{H} (\text{Na})$



1st ionisation energy, $\Delta_{\text{IE}1} \text{H} (\text{Na})$

'This is the enthalpy change that accompanies the **removal of 1 electron** from each atom in **1 mole of gaseous atoms**'

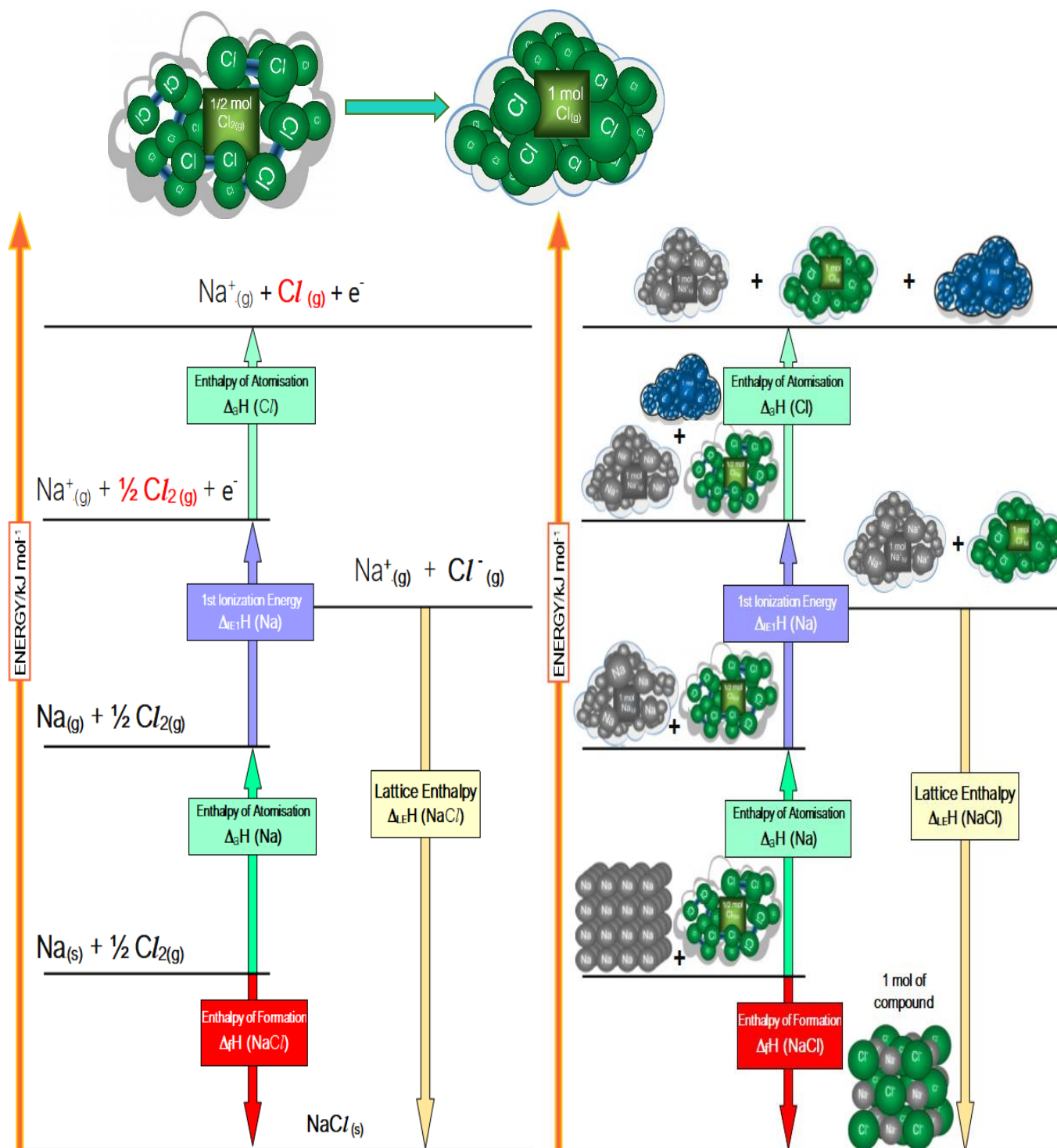
This enthalpy change is always endothermic.



Elemental **chlorine molecules** now need to become **gaseous chlorine atoms** before they can be ionised.

The enthalpy change for this process is the **enthalpy of atomisation**. $\Delta_a H (\text{Cl}_2)$

We require 1 mole of gaseous chlorine atoms so we must break up $\frac{1}{2}$ mole of chlorine molecules to achieve this. You must remember that this enthalpy change is all about 1 mole of atoms made.

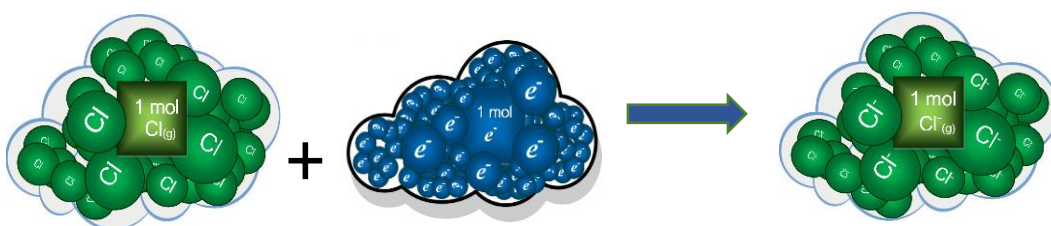


Gaseous chlorine atoms need to become gaseous chloride ions by receiving electrons

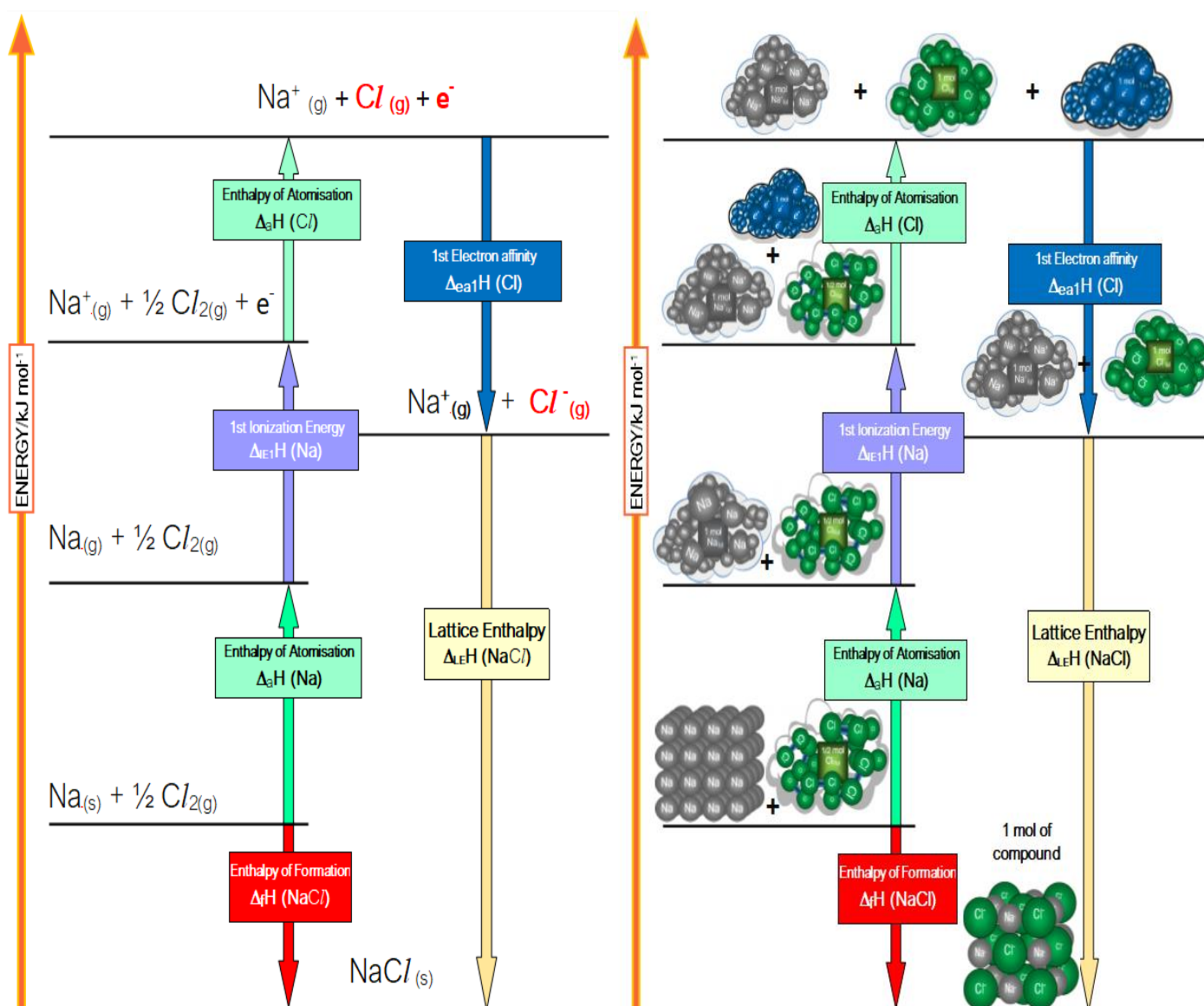
The enthalpy change for this process is the 1st electron affinity, $\Delta_{\text{ea}1}\text{H}(\text{Cl})$

'This is the enthalpy change that accompanies the gaining of 1 electron by each atom in 1 mole of gaseous atoms'

This is clearly very similar to 1st Ionization Energy but involves gain of electrons.



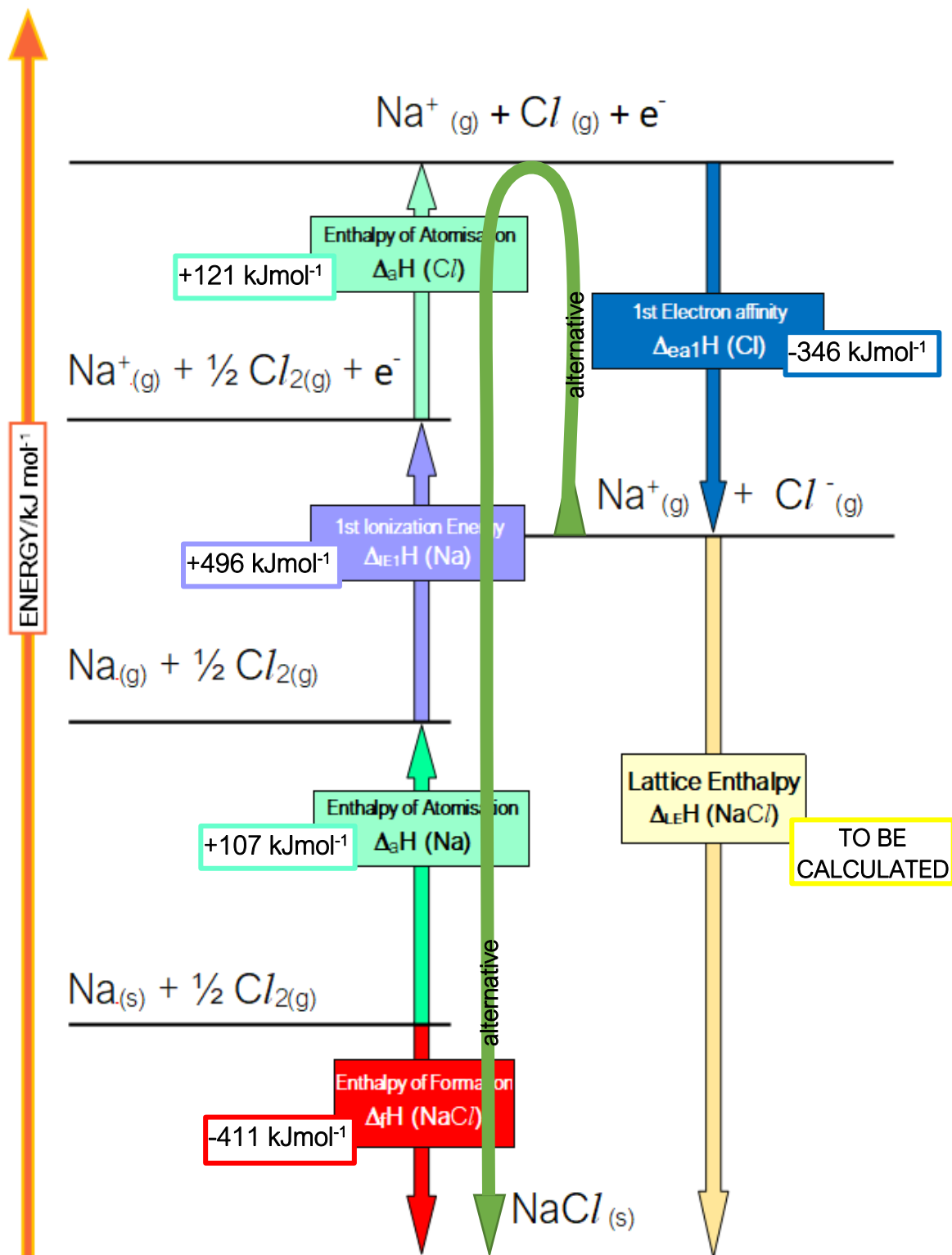
This enthalpy change is the last one and completes our alternative route!



So, we now have a full cycle that will allow us to use experimental data to determine $\Delta_{LEH}(\text{NaCl})$.

I have inserted values for the enthalpy changes.

Born-Haber Cycle for Sodium Chloride



We now need to lay out our calculation **methodically and carefully**. There is a primer on laying out Enthalpy Change Calculations on [CramNow](#)

There are 5 enthalpy changes to 'travel along' on our alternative route.

$$\Delta_{\text{LE}}H(\text{NaCl}) = (-\Delta_{\text{ea}1}H(\text{Cl})) + (-\Delta_{\text{a}}H(\text{Cl}_2)) + (-\Delta_{\text{IE}1}H(\text{Na})) + (-\Delta_{\text{a}}H(\text{Na})) + (+\Delta_{\text{f}}H(\text{NaCl}))$$

All these enthalpy changes have -ve in front of them because the enthalpy change 'journey', takes us in the opposite direction to the arrows.

Inserting all the values and signs:

$$\Delta_{\text{LE}}H(\text{NaCl}) = (-346) + (-121) + (-496) + (-107) + (-411)$$

So,

$$\Delta_{\text{LE}}H(\text{NaCl}) = (+346) + (-121) + (-496) + (-107) + (-411) = -789 \text{ kJmol}^{-1}$$

$$\text{Lattice Enthalpy of NaCl, } \Delta_{\text{LE}}H(\text{NaCl}) = -789 \text{ kJmol}^{-1}$$

The value based on **experimental** data (not theory) is: -789 kJmol^{-1}

The value based on **theoretical** calculations (assuming a perfect ionic model) is -777 kJmol^{-1}

The difference between the two values is only around **1.5%**.

Question:

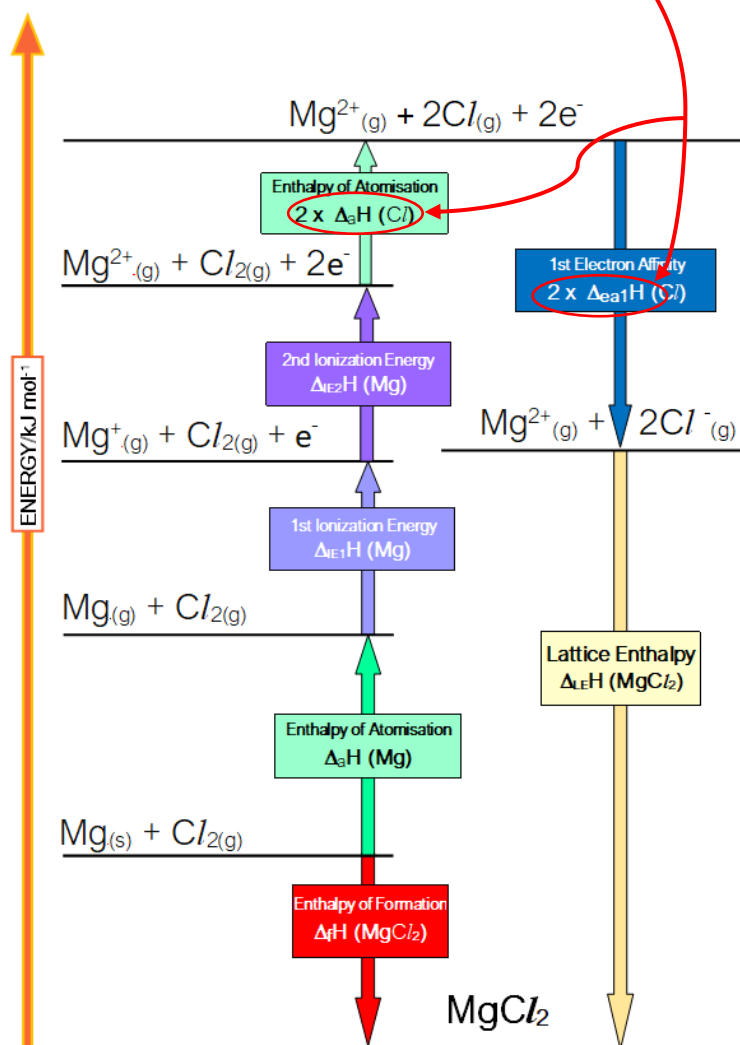
As a scientist, do you feel confident that these values are so close that it supports the idea of a perfect ionic lattice, *i.e.* with point charges? Or, do you feel that this difference casts doubt on the purely ionic model?

More on this later!

Born-Haber Cycle for Magnesium Chloride, MgCl_2

Presented below is the B-H Cycle for magnesium chloride. When calculating the Lattice Enthalpy for magnesium chloride, you can easily fall into a couple of traps.

Firstly, you may well forget that the calculation requires there to be **2 moles of chloride ions made**. Therefore, you will need to produce **2 moles of chlorine atoms** (from 1 mole of molecules). You must remember to double the $\Delta_a\text{H}(\text{Cl})$. Then, each mole of chlorine atoms will need to gain 1 mole of electrons and so the $\Delta_{\text{ea}1}\text{H}(\text{Cl})$ value must also be doubled. **Students routinely forget to double these values!** Don't fall into the trap! You've been warned.



There are 6 enthalpy changes to 'travel along' on our alternative route.

$$\Delta_{\text{LE}}\text{H}(\text{MgCl}_2) = (-2 \times \Delta_{\text{ea}1}\text{H}(\text{Cl})) + (-2 \times \Delta_a\text{H}(\text{Cl}_2)) + (-\Delta_{\text{IE}2}\text{H}(\text{Mg})) + (-\Delta_{\text{IE}1}\text{H}(\text{Mg})) + (-\Delta_a\text{H}(\text{Mg})) + (+\Delta_f\text{H}(\text{MgCl}_2))$$

$$\Delta_{\text{LE}}\text{H}(\text{MgCl}_2) = (-2 \times -346) + (-2 \times +121) + (-1451) + (-738) + (-146) + (+642)$$

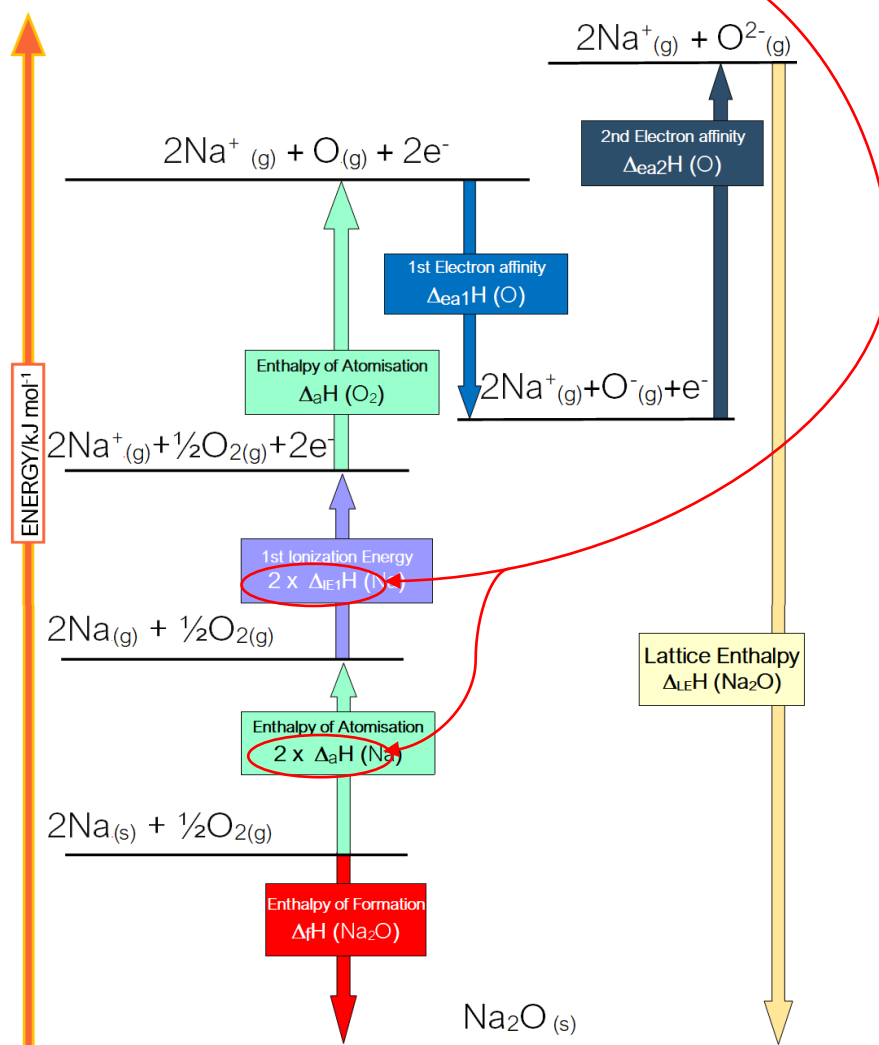
$$\Delta_{\text{LE}}\text{H}(\text{MgCl}_2) = (+692) + (-242) + (-1451) + (-738) + (-146) + (+642) = -2527 \text{ kJ mol}^{-1}$$

$$\text{Lattice Enthalpy of } \text{MgCl}_2, \Delta_{\text{LE}}\text{H}(\text{MgCl}_2) = -2527 \text{ kJ mol}^{-1}$$

Born-Haber Cycle for Sodium Oxide, Na₂O

Presented below is the B-H Cycle for sodium oxide. As with the B-H Cycle for magnesium chloride, when calculating the Lattice Enthalpy for sodium oxide, you can easily fall into some traps.

Firstly, you may well forget that the calculation requires there to be **2 moles of sodium ions made**. Therefore, you will need to produce **2 moles of sodium atoms** from 2 moles of elemental sodium. You must remember to double the $\Delta_a H(\text{Na})$. Then, each mole of sodium atoms will need to lose 1 mole of electrons and so the $\Delta_{IE1} H(\text{Na})$ value must also be doubled. **Students routinely forget to double these values!** Don't fall into the trap! **Again, you've been warned.**



There are 6 enthalpy changes to 'travel along' on our alternative route.

$$\Delta_{LE}H(\text{Na}_2\text{O}) = (-\Delta_{ea2}H(\text{O})) + (-\Delta_{ea1}H(\text{O})) + (\Delta_aH(\text{O})) + (-2 \times \Delta_{IE1}H(\text{Na})) + (-2 \times \Delta_aH(\text{Na})) + (+\Delta_fH(\text{Na}_2\text{O}))$$

$$\Delta_{LE}H(\text{Na}_2\text{O}) = (- +790) + (- -141) + (- +249) + (- 2 \times +496) + (- 2 \times +107) + (+ -414)$$

$$\Delta_{LE}H(\text{Na}_2\text{O}) = (-790) + (+141) + (-249) + (-992) + (-214) + (-414) = -2518 \text{ kJmol}^{-1}$$

$$\text{Lattice Enthalpy of Na}_2\text{O, } \Delta_{LE}H(\text{Na}_2\text{O}) = -2518 \text{ kJmol}^{-1}$$

The other interesting feature for this B-H Cycle, is the **second electron affinity of oxygen**, $\Delta_{ea2}H(O)$. It is clearly significantly endothermic. This is not that surprising as the 2nd electron affinity involves adding electrons to already negative ions ($O^-_{(g)}$) and so the **repulsion needs to be overcome**. Energy needs to be put in to bring this about.

At GCSE, chemistry teachers (including me) often use over simplified language, such as, "Oxygen is an atom in group 6 so it gains 2 electrons in reactions because it *wants* to fill its shell."

We do this because it helps students remember that group 6 elements form ions with a 2- charge. But the idea that oxygen 'wants to gain 2 electrons' is simply incorrect. This is not just because atoms don't have feelings but, more significantly, it actually **takes energy input for oxygen atoms fill their shell**. If anything, it seems that they don't 'want' to fill their second shell!

Just because the formula of sodium oxide is Na_2O and contains Na^+ and O^{2-} doesn't mean that these atoms 'wanted to lose 1 and gain 2 electrons' respectively. This will be explored on the next page.

Use of Born-Haber Cycles to Help Explain Ionic Formulae

Question: Why is the formula of magnesium chloride, MgCl_2 ?

When I ask this question, I can be confident that I will get the following answer, or something similar.

“Magnesium is in group 2 so its atoms want to lose 2 electrons and chlorine is in group 7 so its atoms want to gain one electron. This makes the magnesium ions have a 2+ charge and the sodium ions have a 1+ charge. The charges must balance and therefore the formula is MgCl_2 .”

This is **a great way to predict an ionic formula, but it isn't the reason** for the formula being MgCl_2 .

The way to understand why the empirical formula is MgCl_2 and not MgCl or MgCl_3 is to use a Born-Haber cycle.

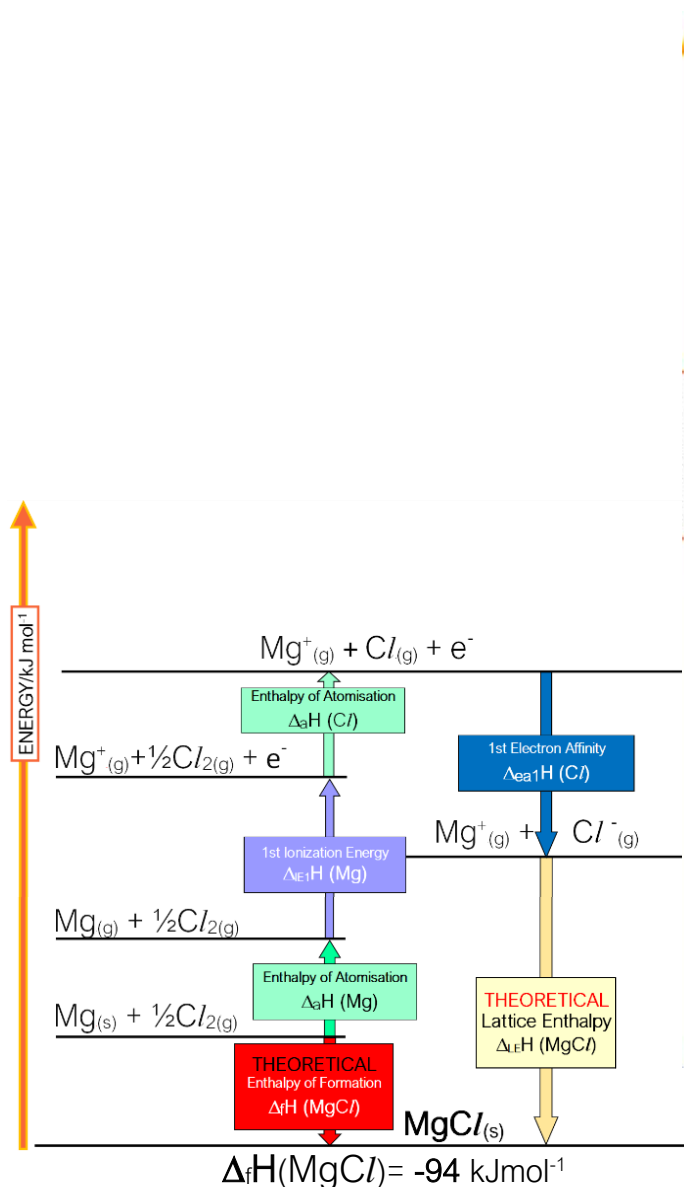
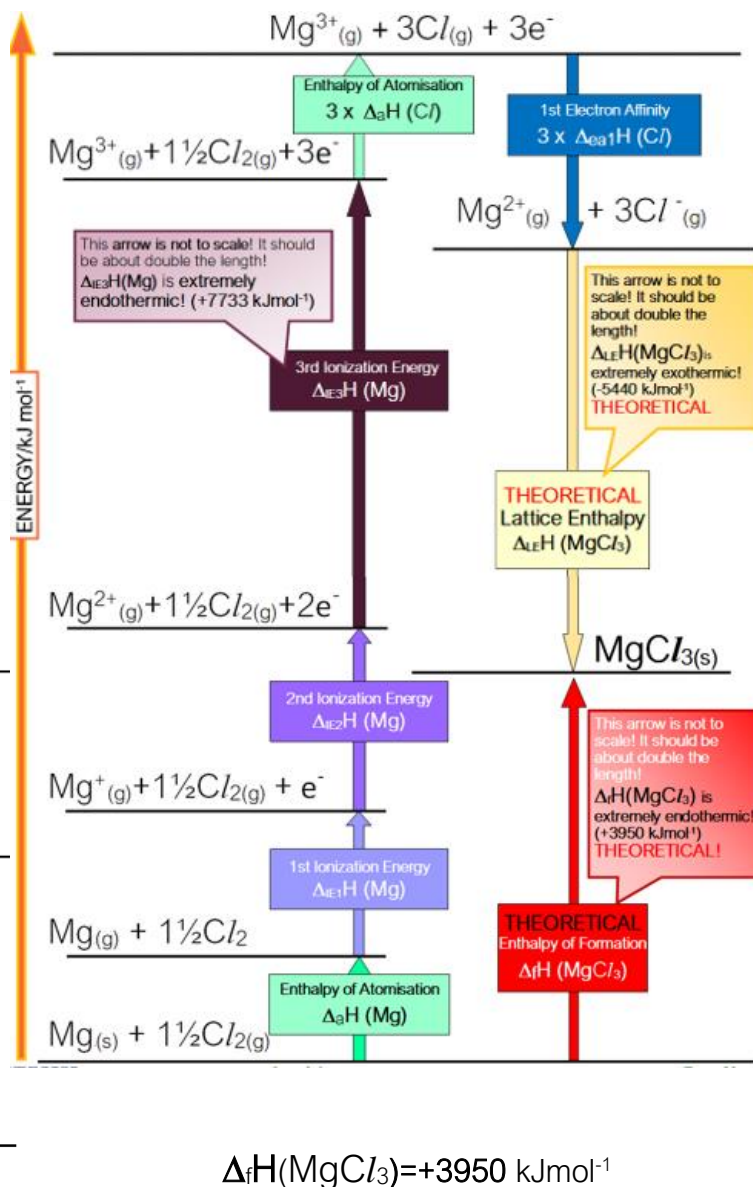
Instead of using the cycle to calculate the Lattice Enthalpy, we will be using the cycle to **calculate a theoretical enthalpy of formation**. We will then compare the enthalpies of formation for MgCl_2 , MgCl and MgCl_3

You may be wondering where the Lattice Enthalpy for the theoretical compounds, MgCl and MgCl_3 will come from. After all, we will need a value of Lattice Enthalpy to be able to calculate the theoretical enthalpies of formation for MgCl and MgCl_3 . For this, we will need to use the value for the Lattice Enthalpy that is given by using the 'physics' method, *i.e.* using the approximation based on the equation.

$$\text{Force} = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2}$$

We have already established that this is an imperfect way of determining Lattice Enthalpy because it makes that assumption that the lattice is purely ionic, which it isn't. However, it will be satisfactory for our purposes, here.

On the following page, there are two Born-Haber cycles for calculating the Enthalpy of Formation of MgCl and MgCl_3 .

Born-Haber Cycle for $MgCl$ Born-Haber Cycle for $MgCl_3$ 

Let's compare these two values with the enthalpy of formation of $MgCl_2$. $\Delta_fH(MgCl_2) = -642 \text{ kJ mol}^{-1}$

It is clear that the enthalpy of formation of $MgCl_2$ is by far the most exothermic of the three values.

If you have already learned something about thermodynamics, you will be aware that there is a strong link between the enthalpy of formation of a compound and its stability. In general, **compounds with exothermic enthalpies of formation are more stable** than those with endothermic enthalpies of formation. The greater the values, the greater the stability or instability respectively.

Following this logic, of the three possible compounds, $MgCl_2$ is the compound that is ultimately formed.

Interestingly, it is thought that $MgCl$ forms initially and this then disproportionates into the more stable compound, $MgCl_2$.



It would be a good idea to look at each Born-Haber cycle to be clear in your own mind, which of the enthalpy changes is the biggest contributing factor that makes the enthalpies of formation of $MgCl$ and $MgCl_3$ so unfavourable.

So, as you can see, the reason for empirical formula of magnesium chloride being $MgCl_2$ is not because magnesium 'wants' to lose 2 electrons and because chlorine 'wants' to lose 1 electron etc., etc.

Challenging the Idea of Pure Ionic Bonding

At GCSE, we usually tell student that there are 2 mains types of bonding in compounds; IONIC and COVALENT.

We often state that *compounds that contain metals, e.g. NaCl, will contain ions and are therefore IONICALLY bonded*. Compounds formed between non-metals, e.g. CH₄ will form molecules where electron pairs are shared between atoms in a perfectly equal way.

This very simplistic model of bonding is satisfactory for explaining all that is required at GCSE. However, at A level, the understanding of chemical bonding needs to be made more sophisticated if we are to explain properties of substances such as aluminium chloride, AlCl₃ which clearly exhibits characteristics that are very different to typical ionic compounds. These physical properties include subliming at relatively low temperature and chemically, it reacts with water. The only way that these properties can be explained is if we can appreciate that aluminium chloride is not purely ionic but is, in fact, more covalent in nature. This simple example instantly dismisses any idea that 'all compounds that contain metals must be ionic', a rule often handed out in GCSE Chemistry.

Early in this document, you will recall that the Lattice Enthalpy can be calculated by two different methods; one method is based on experimental data and a Born-Haber cycle and the other is theoretical, assuming that the ions in an ionic lattice are point charges. The latter calculation considers the lattice to be purely ionic in nature.

For NaCl, the values calculated by each method are pretty close.

The value based on **experimental** data (not theory) is: **-789 kJmol⁻¹**

The value based on **theoretical** calculations (assuming a perfect ionic model) is **-777 kJmol⁻¹**

The difference between the two values is only around **1.5%**.

You could look at this and argue that the values are very similar and therefore accept that the idea that the pure ionic model is supported. But, you are probably more likely, as a scientist, to find out if this comparison holds up for other examples. Presented below are some more examples where the '**experimental**' and '**theoretical**' values are compared. There is also a collection of some other lattice enthalpies that are useful for comparison.

example	Compound	Theoretical Value/ kJmol ⁻¹	Experimental Value/ kJmol ⁻¹	% Difference	Compound
1	NaCl	-777	-789	1.5	NaCl
2	NaBr	-732	-751	2.6	NaBr
3	NaI	-682	-705	3.4	NaI
4	KCl	-702	-711	1.3	KCl
5	KBr	-667	-682	2.2	KBr
6	KI	-636	-651	2.4	KI
7	CsF	-744	-759	2.0	CsF
8	CsCl	-657	-670	2.0	CsCl
9	CsI	-600	-613	2.2	CsI
10	AgF	-920	-958	4.1	AgF
11	AgCl	-833	-905	8.6	AgCl
12	AgI	-778	-889	14.1	AgI
13	MgF ₂		-2913		MgF ₂
14	MgCl ₂		-2526		MgCl ₂
15	CaCl ₂		-2258		CaCl ₂
16	BeO		-4443		BeO
17	MgO		-3791		MgO
18	MgS		-3406		MgS

Things to Consider from the Data

1. All the experimental values of enthalpy changes are greater than the theoretical values for the same compound.

This suggests that the bonds in the compound are stronger than they would be if the compound was purely ionic. A suggested explanation is that there is some **additional covalent bonding** adding to the ionic bonding

2. The percentage difference between the experimental values of enthalpy changes and the theoretical values increases as the difference in electronegativity between the two elements in the compound decreases.

This suggests that the bonds become less ionic and more covalent as the difference in electronegativity decreases. We conclude that there are no purely ionic compounds. Instead, there is a sliding scale of covalency.

3. By considering groups of compounds (groups linked by their coloured backgrounds in the table) we can see that there are clear correlations between the **size of the anions** in the compounds and the size of the enthalpy change.

In all the cases, **the larger the halide anion, the smaller the enthalpy change.**

4. If we now fix the size of the **anion** by selecting chloride, we can compare the lattice enthalpies of **NaCl, KCl, CsCl**

We can see that there is another clear correlation between the **size of the cation** in the compounds and the size of the enthalpy change.

In all the cases, **the larger the cation, the smaller the enthalpy change.**

Look through the examples **13-18** to see if this relationship between the size of **anions** and **cations** still holds up!

5. We will now consider the effect of the **charge of the cations** on the lattice enthalpy. To do this we can select two different chlorides, **NaCl** and **MgCl₂**. These are examples, 1 and 14.

Na^+ and Mg^{2+} have reasonably similar ionic radii so the size is effectively constant.

The size of the enthalpy change is significantly different, **MgCl₂**, having a far larger value.

We can repeat this by comparing **KCl** and **CaCl₂**. The pattern is repeated, **CaCl₂** having a far larger value.

The larger the charge on the cation, the larger the lattice enthalpy.

6. We will now consider the effect of the **charge of the anions** on the lattice enthalpy. To do this we can select two different magnesium compounds, **MgF₂** and **MgO**. These are examples, 14 and 17.

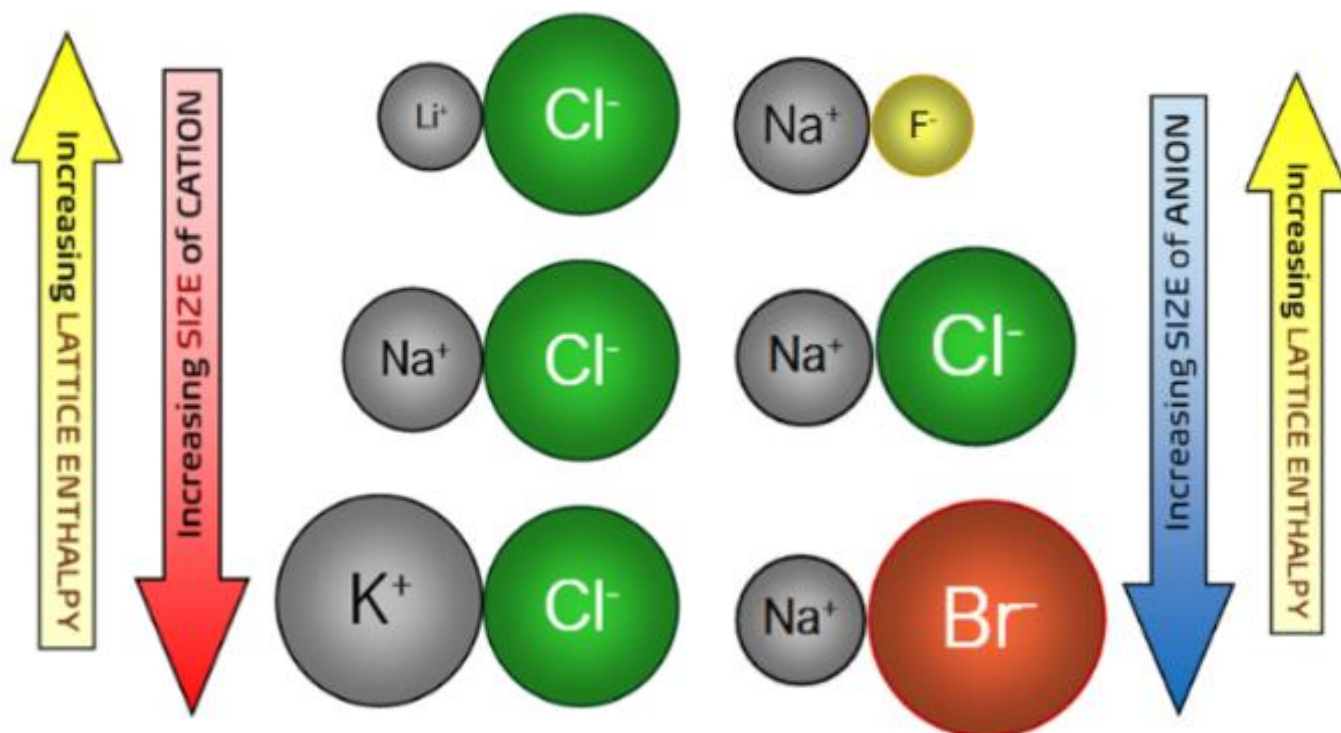
F^- and O^{2-} have similar ionic radii so the size is effectively constant.

The size of the enthalpy change is significantly different, **MgO**, having a far larger value.

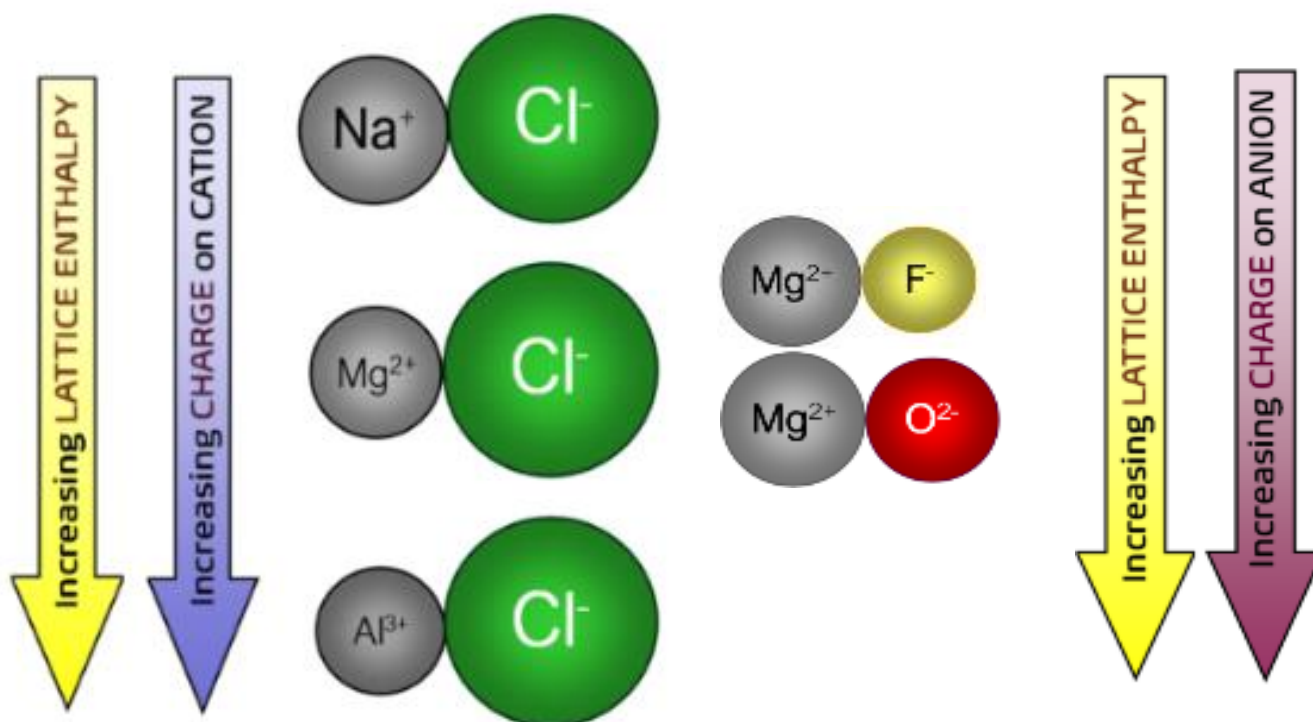
The larger the charge on the anion, the larger the lattice enthalpy.

In summary:

Effect of the SIZE of IONS on LATTICE ENTHALPY, Δ_{LEH}



Effect of the the SIZE of IONIC CHARGE on the size of LATTICE ENTHALPY, Δ_{LEH}



Comparison of Atomic and Ionic Radii for a Range of Elements.

The atoms are coloured grey. **Cations** are red and **anions** are blue. Radii are measured in pm (10^{-12} m)

GROUP 1		GROUP 2		GROUP 3		GROUP 6		GROUP 7	
Li^+ 90	Li 134	Be^{2+} 59	Be 90	B^{3+} 41	B 82	O 73	O^{2-} 126	F 71	F^- 119
Na^+ 116	Na 154	Mg^{2+} 86	Mg 130	Al^{3+} 68	Al 118	S 102	S^{2-} 170	Cl 99	Cl^- 167
K^+ 152	K 196	Ca^{2+} 114	Ca 174	Ga^{3+} 76	Ga 126	Se 116	Se^{2-} 184	Br 114	Br^- 182
Rb^+ 166	Rb 211	Sr^{2+} 132	Sr 192	In^{3+} 94	In 144	Te 135	Te^{2-} 207	I 133	I^- 206

This diagram and data were taken from Wikipedia.

You should now try to construct a Born-Haber Cycle to calculate the Lattice Enthalpy for **potassium fluoride**, $\Delta_{\text{LE}}H(\text{KF})$. All the necessary data can be found in the data tables in the **TOOLS**.