🧪 Cambridge (CIE) A Level Chemistry

Lattice Energy & Born–Haber Cycles

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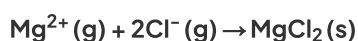
Lattice Energy & Enthalpy Change of Atomisation

- **Enthalpy change** (ΔH) refers to the amount of heat energy **transferred** during a chemical reaction, at a constant pressure

Lattice energy

- The **lattice energy** ($\Delta H_{latt}^{\ominus}$) is:

The enthalpy change when 1 mole of an ionic compound is formed from its gaseous ions (under standard conditions)

- The $\Delta H_{latt}^{\ominus}$ is always **exothermic,** as when ions are **combined** to form an **ionic solid lattice** there is an extremely large release of energy

    - The enthalpy change will always have a **negative** value

    - Because of the huge release in energy when the gaseous ions combine, the value will be a very **large negative** value

- The large negative value of $\Delta H_{latt}^{\ominus}$ suggests that the **ionic compound** is much more **stable** than its **gaseous ions**

    - This is due to the **strong electrostatic forces of attraction** between the oppositely charged ions in the solid lattice

    - Since there are no electrostatic forces of attraction between the ions in the gas phase, the gaseous ions are **less stable** than the ions in the **ionic lattice**

    - The **more exothermic** the value is, the **stronger the ionic bonds** within the lattice are

- The $\Delta H_{latt}^{\ominus}$ of an ionic compound **cannot** be determined **directly** by one single experiment

- Multiple experimental values and an **energy cycle** are used to find the $\Delta H_{latt}^{\ominus}$ of ionic compounds

- The lattice energy ($\Delta H_{latt}^{\ominus}$) of an ionic compound can be written as an equation

    - E.g. magnesium chloride is an ionic compound formed from magnesium (Mg^{2+}) and chloride (Cl^-) ions:

$$Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$$

> ### ✎ Worked Example
>
> Write the equations which represent the lattice energy of:

1. Magnesium oxide

2. Lithium chloride

Answer 1:

- $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$

Answer 2:

- $Li^{+}(g) + Cl^{-}(g) \rightarrow LiCl(s)$
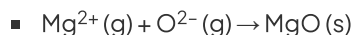
Enthalpy change of atomisation

- The **standard enthalpy change of atomisation** ($\Delta H_{at}^{\ominus}$) is:

The enthalpy change when 1 mole of gaseous atoms is formed from its element under standard conditions

- The $\Delta H_{at}^{\ominus}$ is always **endothermic** as energy is always required to **break** any bonds between the atoms in the element into its gaseous atoms

  - Since this is always an endothermic process, the enthalpy change will always have a **positive** value

- Equations can be written to show the standard enthalpy change of atomisation ($\Delta H_{at}^{\ominus}$) for elements

  - E.g. The standard enthalpy change of atomisation for sodium is the energy required to form 1 mole of **gaseous** sodium atoms:

$$Na(s) \rightarrow Na(g) \quad \Delta H_{at}^{\ominus} = +107 \text{ kJ mol}^{-1}$$
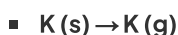
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Worked Example

Write the equations for the standard enthalpy change of atomisation, ($\Delta H_{at}^{\ominus}$) for:
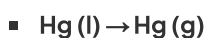
1. Potassium

2. Mercury

Answer 1:

- Potassium in its elemental form is a **solid**, therefore the standard enthalpy change of atomisation is the energy required to form 1 mole of K (g) from K (s)

  - $K(s) \rightarrow K(g)$

Answer 2:

- Mercury in its elemental form is a **liquid**, so the standard enthalpy change of atomisation of mercury is the energy required to form 1 mole of Hg (g) from Hg (l)

  - $Hg(l) \rightarrow Hg(g)$

Examiner Tips and Tricks

Standard conditions in this syllabus are a temperature of 298 K and a pressure of 101 kPa

Make sure the correct **state symbols** are stated when writing these equations – it is crucial that you use these correctly throughout this entire topic
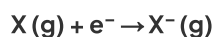
Your notes

Electron Affinity

Electron affinity

- The **first electron affinity** (**EA$_1$**) is the enthalpy change when **1 mole** of **electrons** is added to **1 mole** of **gaseous atoms,** to form **1 mole** of **gaseous ions** each with a single **negative** charge under standard conditions

$$X\,(g) + e^- \rightarrow X^-\,(g)$$

- EA$_1$ is usually **exothermic,** as energy is released

- The value for EA$_1$ will usually be **negative**

- An element can also accept more than one electron, in which case **successive electron affinities** are used

  - For example, the **second electron affinity** (EA$_2$) and **third electron affinity** (EA$_3$) of an element represent the formation of 1 mole of gaseous ions with 2– and 3– charges respectively

- The **second** and **third** electron affinities are **endothermic,** as energy is absorbed

  - This is because the **incoming electron** is added to an **already negative ion**

  - Energy is required to overcome the **repulsive forces** between the incoming electron and negative ion

  - The values will be **positive**

Second & third electron affinity summary

- EA$_1$

  - $X\,(g) + e^- \rightarrow X^-\,(g)$

  - Exothermic

- EA$_2$

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

  - Endothermic

- EA$_3$

  - $X^{2-}\,(g) + e^- \rightarrow X^{3-}\,(g)$

  - Endothermic

Factors affecting electron affinity

The **electron affinity** of an element depends on how strongly the nucleus attracts an incoming electron.

- The **stronger the attraction** between the nucleus and the incoming electron, the **more energy is released**, making the electron affinity more **exothermic (more negative)**

- The factors that affect electron affinity are the same as those that influence ionisation energy:

- Nuclear charge

  - A **higher nuclear charge** means a stronger pull on the incoming electron, resulting in a more exothermic electron affinity

- Distance (atomic radius)

  - A **larger distance** between the nucleus and the outermost shell reduces the attractive force, making electron affinity less exothermic

- Shielding

  - More **inner electron shells** increase shielding, which **weakens the nuclear attraction** for the incoming electron, leading to a less exothermic electron affinity

Trends in electron affinity of Group 16 & Group 17 elements

- Electron affinities of **non-metals** become **more exothermic** across a **period,** with a maximum at Group 17

- There is generally a downwards trend in the size of the electron affinities of the elements in Group 16 and 17

  - The electron affinities generally become **less exothermic** for each successive element going down both Groups, apart from the first member of each Group (oxygen and fluorine respectively)

Electron affinity table

Electron Affinity / kJ mol^{-1}	
Group 16	Group 17
O = −141	F = −328
S = −200	Cl = −345
Se = −195	Br = −325
Te = −190	I = −295

- An atom of **chlorine** has a higher nuclear charge than sulfur

  - This stronger nuclear charge results in a greater attraction between the nucleus and the incoming electron
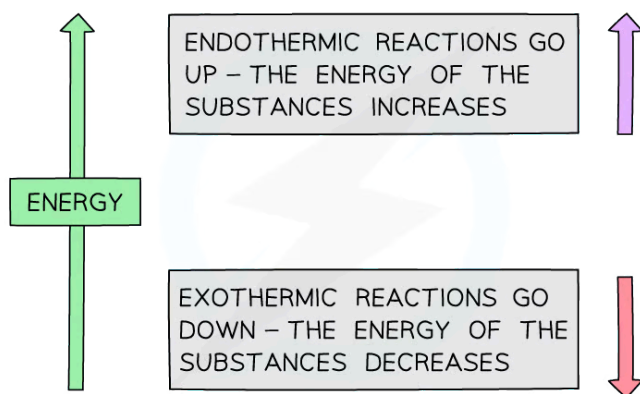
- Therefore, **more energy is released** when an electron is added to chlorine, making its first electron affinity (**EA$_1$**) **more exothermic** than that of sulfur
- As you move down Group 16 or Group 17:
    - The **outermost electrons are farther from the nucleus**, so the attractive force is weaker
    - There are **more electron shells**, increasing shielding and further reducing nuclear attraction
    - It becomes **more difficult to add an electron** to the outer shell
    - **Less energy is released**, so the electron affinity becomes **less exothermic**
- **Fluorine** as an exception
    - Fluorine has a **very small atomic radius**, resulting in:
    - High electron density around the nucleus.
    - Increased repulsion between the incoming electron and the existing electrons.
    - This repulsion weakens the overall attraction to the nucleus.
    - As a result, fluorine's first electron affinity is **less exothermic than expected**, and it is actually lower than that of chlorine.

Constructing Born-Haber Cycles

- A **Born-Haber cycle** is a specific application of **Hess's Law** for ionic compounds and enable us to calculate lattice enthalpy which cannot be found by experiment

- The basic principle of drawing the cycle is to construct a diagram in which energy increases going up the diagram

The basic principle of a Born-Haber cycle

ENDOTHERMIC REACTIONS GO UP – THE ENERGY OF THE SUBSTANCES INCREASES

ENERGY

EXOTHERMIC REACTIONS GO DOWN – THE ENERGY OF THE SUBSTANCES DECREASES

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The direction of the arrows in Born-Haber cycles indicates if a reaction is exothermic or endothermic

- The cycle shows all the steps needed to turn atoms into gaseous ions and from gaseous ions into the ionic lattice

- The alternative route to the ionic lattice begins from the enthalpy of formation of the elements in their standard states

Drawing the cycle for sodium chloride

- A good starting point is to draw the elements with their state symbols about a third of the way up the diagram

- This is shown as the left-hand side of the equation for the process indicated

- The location is marked by drawing a horizontal bar or line which represents the starting energy level

Drawing a Born-Haber cycle step 1

THE GASEOUS IONS WILL BE HERE

$Na (s) + \frac{1}{2}Cl_2(g)$

THE IONIC SOLID WILL BE HERE
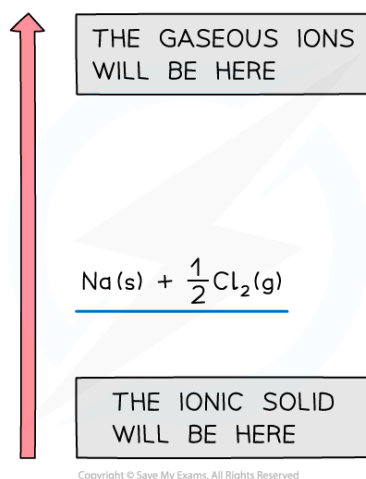
- Next, we need to create the gaseous ions

- This is a two-step process of first creating the gaseous atoms and then turning them into ions

- Creating gaseous atoms is a bond-breaking process, so arrows must be drawn upwards

- It doesn't matter whether you start with sodium or chlorine

- The enthalpy of atomisation of sodium is

$$Na (s) \rightarrow Na (g) \qquad \Delta H_{at}^{\theta} = +108 \, kJ \, mol^{-1}$$

- The enthalpy of atomisation of chlorine is

$$\tfrac{1}{2}Cl_2 (g) \rightarrow Cl (g) \qquad \Delta H_{at}^{\theta} = +121 \, kJ \, mol^{-1}$$
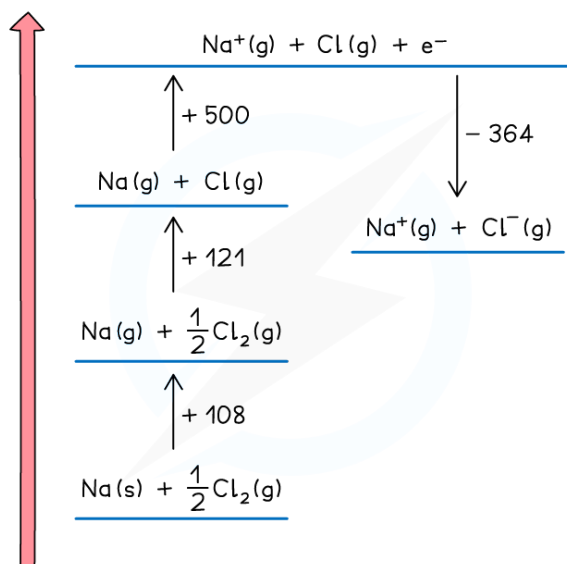
- We can show the products of the process on the horizontal lines and the energy value against a vertical arrow connecting the energy levels

Drawing a Born–Haber cycle step 2 – creating the gaseous atoms

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- Now the ions are created

- The sodium ion loses an electron, so this energy change is the first ionisation energy for sodium

$$Na\,(g) \rightarrow Na^+\,(g) + e^- \qquad \Delta H_{ie}^{\theta} = +500 \text{ kJ mol}^{-1}$$

- The change is endothermic so the direction continues upwards

- The chlorine atom gains an electron, so this is electron affinity

$$Cl\,(g) + e^- \rightarrow Cl^-\,(g) \qquad \Delta H_{ea}^{\theta} = -364 \text{ kJ mol}^{-1}$$
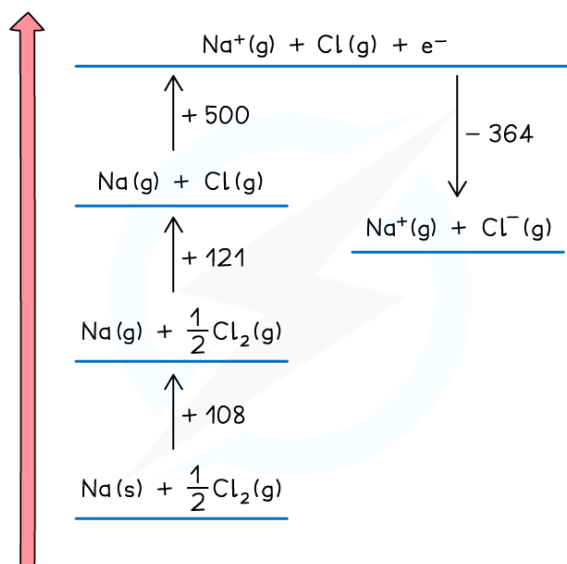
- The exothermic change means this is downwards

- The change is displaced to the right to make the diagram easier to read

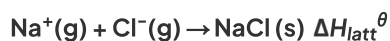## Drawing a Born–Haber cycle step 3 – creating the gaseous ions

Na$^+$(g) + Cl(g) + e$^-$

+ 500

- 364

Na(g) + Cl(g)

+ 121

Na$^+$(g) + Cl$^-$(g)

Na(g) + $\frac{1}{2}$Cl$_2$(g)

+ 108

Na(s) + $\frac{1}{2}$Cl$_2$(g)

- The two remaining parts of the cycle can now be completed

- The enthalpy of formation of sodium chloride is added at the bottom of the diagram

$$Na(s) + \tfrac{1}{2}Cl_2\,(g) \rightarrow NaCl\,(s) \qquad \Delta H_f^{\theta} = -411\,kJ\,mol^{-1}$$

- This is an exothermic change for sodium chloride so the arrow points downwards

- Enthalpy of formation can be exothermic or endothermic, so you may need to show it above the elements (and displaced to the right) for a endothermic change

- The final change is lattice enthalpy, which is usually shown a formation. For sodium chloride the equation is

$$Na^+(g) + Cl^-(g) \rightarrow NaCl\,(s) \; \Delta H_{latt}^{\theta}$$

Drawing a Born–Haber cycle step 4 – completing the cycle
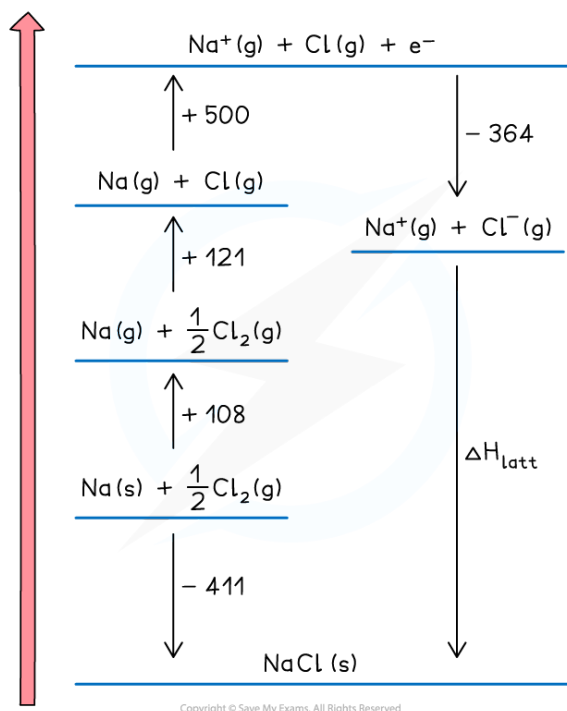
- The cycle is now complete

- The cycle is usually used to calculate the lattice enthalpy of an ionic solid, but can be used to find other enthalpy changes if you are given the lattice enthalpy
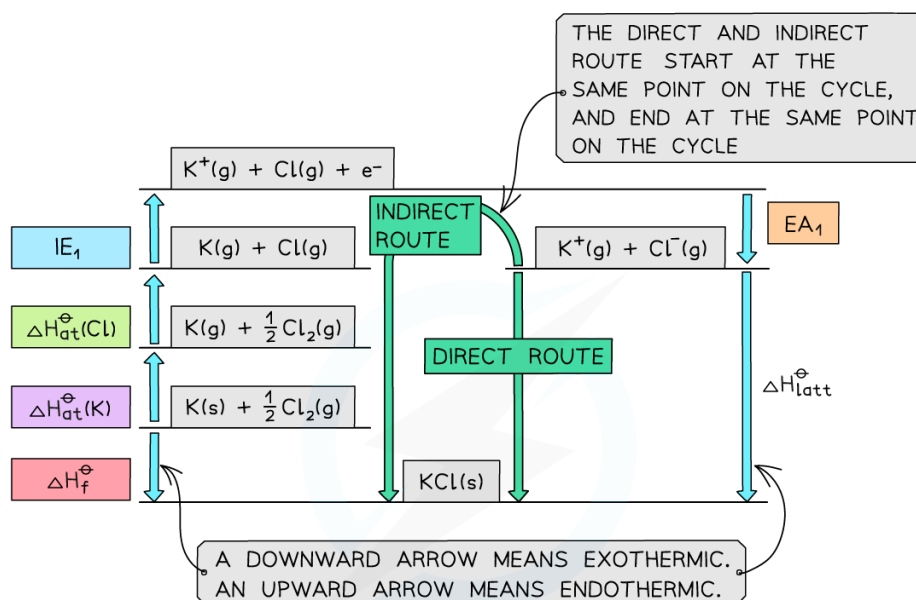
Worked Example

Construct a Born–Haber Cycle which can be used to calculate the lattice energy of potassium chloride.

Step	Equation	Enthalpy Change
Convert K (s) atoms into K (g) atoms	K (s) $\rightarrow$ K (g)	$\Delta H_{at}{}^{\theta}$
Convert K (g) atoms into K$^+$ (g) ions	K (g) $\rightarrow$ K$^+$ (g)	IE_1
Convert Cl$_2$ (g) molecules into Cl (g) atoms	½Cl$_2$ (g) $\rightarrow$ Cl (g)	$\Delta H_{at}{}^{\theta}$
Convert Cl (g) atoms into Cl$^-$ (g) ions	Cl (g) + e$^-$ $\rightarrow$ Cl$^-$ (g)	EA_1
Add up all values to get $\Delta H_1{}^{\theta}$		$\Delta H_1{}^{\theta}$
Apply Hess's Law to find $\Delta H_{latt}{}^{\theta}$		$\Delta H_{latt}{}^{\theta}$

Answer:

THE DIRECT AND INDIRECT ROUTE START AT THE SAME POINT ON THE CYCLE, AND END AT THE SAME POINT ON THE CYCLE

$K^+(g) + Cl(g) + e^-$

IE_1 $K(g) + Cl(g)$ **INDIRECT ROUTE** $K^+(g) + Cl^-(g)$ EA_1

$\Delta H^{\ominus}_{at}(Cl)$ $K(g) + \frac{1}{2}Cl_2(g)$

DIRECT ROUTE

$\Delta H^{\ominus}_{at}(K)$ $K(s) + \frac{1}{2}Cl_2(g)$ $\Delta H^{\ominus}_{latt}$

$\Delta H^{\ominus}_f$ $KCl(s)$

A DOWNWARD ARROW MEANS EXOTHERMIC. AN UPWARD ARROW MEANS ENDOTHERMIC.

$$\Delta H^{\ominus}_f = \left(\Delta H^{\ominus}_{at}(K)\right) + \left(\Delta H^{\ominus}_{at}(Cl)\right) + \left(IE_1\right) + \left(EA_1\right) + \left(\Delta H^{\ominus}_{latt}\right)$$

$$\therefore \Delta H^{\ominus}_{latt} = \left(\Delta H^{\ominus}_f\right) - \left(EA_1\right) - \left(IE_1\right) - \left(\Delta H^{\ominus}_{at}(Cl)\right) - \left(\Delta H^{\ominus}_{at}(K)\right)$$

$$\Delta H^{\ominus}_1$$

Worked Example

Construct a Born–Haber Cycle which can be used to calculate the lattice energy of magnesium oxide.

Step	Equation	Enthalpy Change
Convert Mg (s) atoms into Mg (g) atoms	Mg (s) → Mg (g)	ΔH_{at}^{θ}
Convert Mg (g) atoms into Mg$^+$ (g) ions	Mg (g) → Mg$^+$ + e$^-$ (g)	IE_1
Convert Mg$^+$ (g) atoms into Mg^{2+} (g) ions	Mg$^+$ (g) → Mg^{2+} + e$^-$ (g)	IE_2
Convert O$_2$ (g) molecules into O (g) atoms	½O (g) → O (g)	ΔH_{at}^{θ}
Convert O (g) atoms into O$^-$ (g) ions	O (g) + e$^-$ → O$^-$ (g)	EA_1
Convert O$^-$ (g) atoms into O^{2-} (g) ions	O$^-$ (g) + e$^-$ → O^{2-} (g)	EA_2
Add up all values to get ΔH_1^{θ}		ΔH_1^{θ}

Apply Hess's Law to find $\Delta H_{latt}{}^{\theta}$		$\Delta H_{latt}{}^{\theta}$

Answer:

$$\Delta H_f^{\ominus} = \left(\Delta H_{at}^{\ominus}(Mg)\right) + \left(\Delta H_{at}^{\ominus}(O)\right) + \left(IE_1\right) + \left(IE_2\right) + \left(EA_1\right) + \left(EA_2\right) + \left(\Delta H_{latt}^{\ominus}\right)$$

$$\therefore \Delta H_{latt}^{\ominus} = \left(\Delta H_f^{\ominus}\right) - \underbrace{\left(EA_1\right) - \left(EA_2\right) - \left(IE_1\right) - \left(IE_2\right) - \left(\Delta H_{at}^{\ominus}(Mg)\right) - \left(\Delta H_{at}^{\ominus}(O)\right)}_{\Delta H_1^{\ominus}}$$

Calculations Using Born-Haber Cycles

- Once a Born-Haber cycle has been constructed, it is possible to calculate the lattice energy (ΔH_{latt}^{θ}) by applying Hess's law and rearranging:

$$\Delta H_f^{\theta} = \Delta H_{at}^{\theta} + \Delta H_{at}^{\theta} + IE + EA + \Delta H_{latt}^{\theta}$$

If we simplify this into three terms, this makes the equation easier to see:

- ΔH_{latt}^{θ}

- ΔH_f^{θ}

- ΔH_1^{θ} (the sum of all of the various enthalpy changes necessary to convert the elements in their standard states to gaseous ions)

- The simplified equation becomes

$$\Delta H_f^{\theta} = \Delta H_1^{\theta} + \Delta H_{latt}^{\theta}$$

So, if we rearrange to calculate the lattice energy, the equation becomes

$$\Delta H_{latt}^{\theta} = \Delta H_f^{\theta} - \Delta H_1^{\theta}$$

- When calculating the ΔH_{latt}^{θ}, all other necessary values will be given in the question

- A Born-Haber cycle could be used to calculate any stage in the cycle

  - For example, you could be given the lattice energy and asked to calculate the enthalpy change of formation of the ionic compound

  - The principle would be exactly the same

  - Work out the **direct** and **indirect route** of the cycle (the stage that you are being asked to calculate will always be the direct route)

  - Write out the equation in terms of enthalpy changes and rearrange if necessary to calculate the required value

- **Remember:** sometimes a value may need to be doubled or halved, depending on the ionic solid involved

  - For example, with $MgCl_2$ the value for the first electron affinity of chlorine would need to be doubled in the calculation, because there are two moles of chlorine atoms

  - Therefore, you are adding **2 moles** of electrons to **2 moles** of chlorine atoms, to form **2 moles** of Cl^- ions
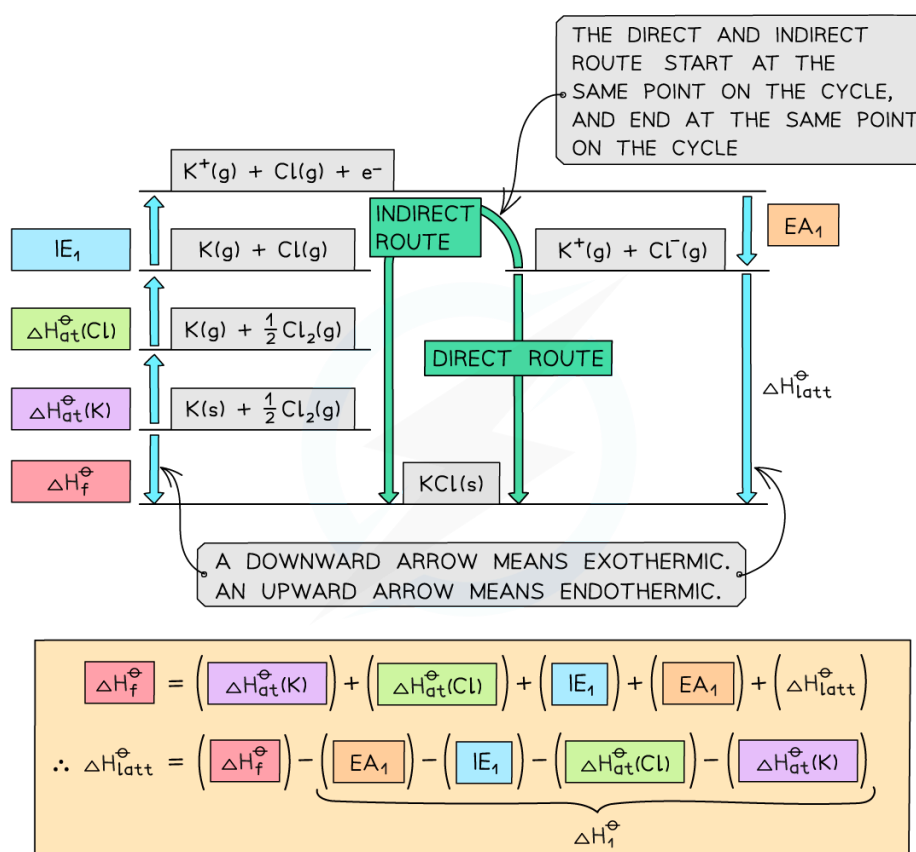
Worked Example

Using the data below, calculate the ΔH_{latt}^{θ} of potassium chloride, KCl.

	ΔH_{at}^{θ} / kJ mol^{-1}	IE / EA / kJ mol^{-1}
K	+90	+418
Cl	+122	−349
ΔH_f^{θ} / kJ mol^{-1}		
KCl	−437	

Answer:

- **Step 1:** The corresponding Born–Haber cycle is:

- **Step 2:** Applying Hess' law, the lattice energy of KCl is:

  - $\Delta H_{latt}^{\theta} = \Delta H_f^{\theta} - \Delta H_1^{\theta}$
  - $\Delta H_{latt}^{\theta} = \Delta H_f^{\theta} - [(\Delta H_{at}^{\theta} \text{ K}) + (\Delta H_{at}^{\theta} \text{ Cl}) + (IE_1 \text{ K}) + (EA_1 \text{ Cl})]$
  - Step 3: Substitute in the numbers:
  - $\Delta H_{latt}^{\theta} = (-437) - [(+90) + \mathbf{(+122) + (+418) + (-349)}] = \mathbf{-718 \text{ kJ mol}^{-1-1}}$

Worked Example

Using the data below, calculate the $\Delta H_{latt}{}^{\theta}$ of magnesium oxide, MgO.

	$\Delta H_{at}{}^{\theta}$ / kJ mol^{-1}	IE_1 / EA_1 / kJ mol^{-1}	IE_2 / EA_2 / kJ mol^{-1}
Mg	+148	+736	+1450
O	+248	−142	+770
$\Delta H_f{}^{\theta}$ / kJ mol^{-1}			
MgO	−602		

Answer:

- **Step 1:** The corresponding Born–Haber cycle is:

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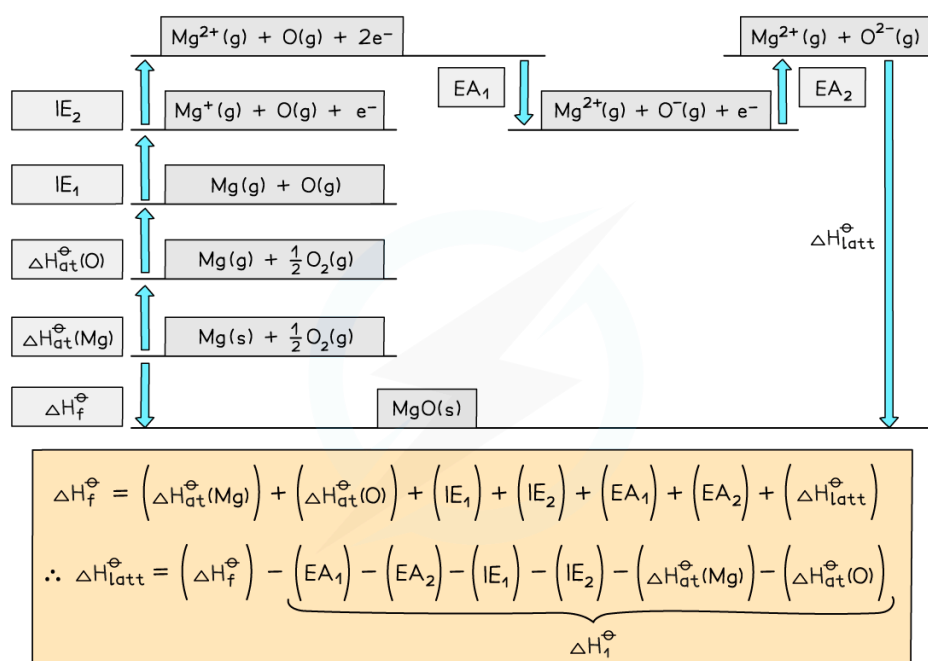
- **Step 2:** Applying Hess' law, the lattice energy of MgO is:

  - $\Delta H_{latt}{}^{\theta} = \Delta H_f{}^{\theta} - \Delta H_1{}^{\theta}$
  - $\Delta H_{latt}{}^{\theta} = \Delta H_f{}^{\theta} - [(\Delta H_{at}{}^{\theta}\ Mg) + (\Delta H_{at}{}^{\theta}\ O) + (IE_1\ Mg) + (IE_2\ Mg) + (EA_1\ O) + (EA_2\ O)]$
  - **Step 3:** Substitute in the numbers:
  - $\Delta H_{latt}{}^{\theta} = (−602) − [(+148) + (+248) + (+736) + (+1450) + (−142) + (+770)]$

Examiner Tips and Tricks

Make sure you use brackets when carrying out calculations using Born–Haber cycles as you may forget a +/− sign which will affect your final answer!
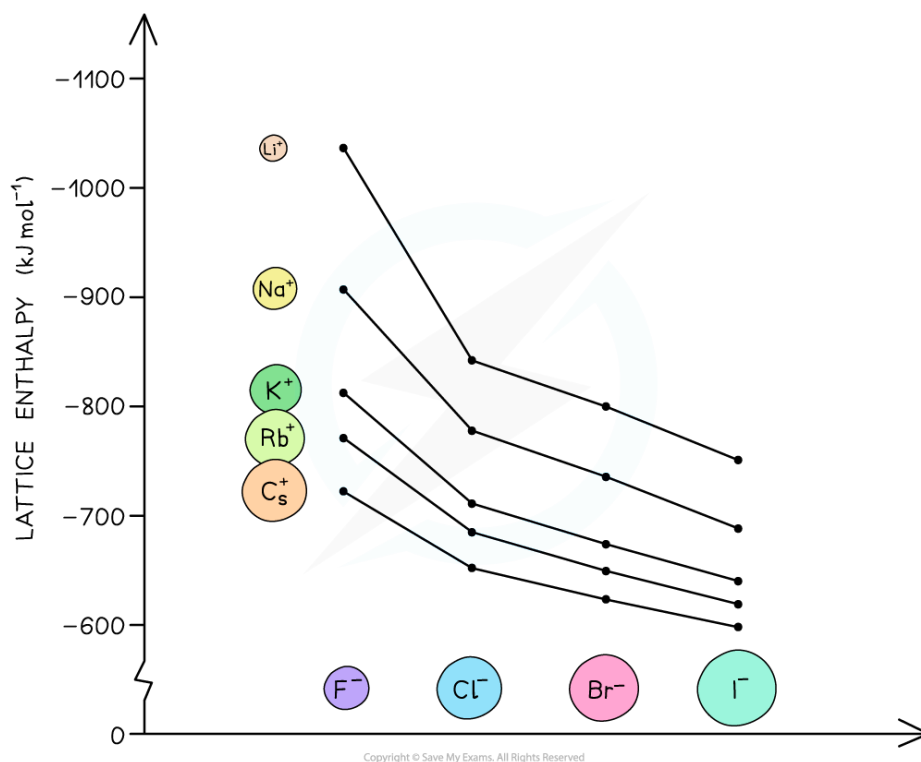
Lattice Energy: Ionic Charge & Radius

- The two key factors which affect lattice energy, $\Delta H_{latt}^{\ominus}$, are the **charge** and **radius** of the ions that make up the **crystalline lattice**

Ionic radius

- The lattice energy becomes **less exothermic** (numerically less negative) as the **ionic radius increases**

    - In larger ions, the **charge is spread over a greater volume**, so **charge density is lower**

    - The ions are also **further apart** in the lattice, increasing the distance between their centres

    - As a result, the **electrostatic attraction between oppositely charged ions is weaker**, and less energy is released when the lattice forms

- For example:

    - Both CsF and KF contain F⁻ ions

    - Cs⁺ is larger than K⁺, so the lattice energy of CsF is **less exothermic** than that of KF

Trends in the lattice energy of different metal halides

The lattice energies get less exothermic as the ionic radius of the ions increases

Ionic charge

The lattice energy becomes **more exothermic** (more negative) as the **ionic charge increases**.

- Higher ionic charge leads to **higher charge density**

- This results in **stronger electrostatic attractions** between oppositely charged ions

- Consequently, **more energy is released** when the lattice is formed

- For example:

  - CaO is composed of Ca^{2+} and O^{2-} ions, while KCl contains K^+ and Cl^- ions

  - The ions in CaO have **higher charges**, so the electrostatic forces are stronger

  - Therefore, the lattice energy of CaO is **more exothermic** than that of KCl

  - Additionally, Ca^{2+} and O^{2-} ions are smaller than K^+ and Cl^-, further increasing the exothermic value