

# Cambridge (CIE) A Level Chemistry



Your notes

## Lattice Energy & Born-Haber Cycles

### Contents

- \* Lattice Energy & Enthalpy Change of Atomisation
- \* Electron Affinity & Trends of Group 16 & 17 Elements
- \* Constructing Born-Haber Cycles
- \* Calculations using Born-Haber Cycles
- \* Factors Affecting Lattice Energy



# Lattice Energy & Enthalpy Change of Atomisation

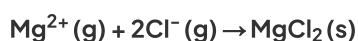
- **Enthalpy change** ( $\Delta H$ ) refers to the amount of heat energy **transferred** during a chemical reaction, at a constant pressure

## 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 ( $\text{Mg}^{2+}$ ) and chloride ( $\text{Cl}^-$ ) ions:



### Worked Example

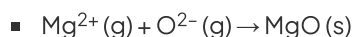
Write the equations which represent the lattice energy of:



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1. Magnesium oxide
2. Lithium chloride

**Answer 1:**



**Answer 2:**



## Enthalpy change of atomisation

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

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

- The  $\Delta H_{\text{at}}^\ominus$  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 ( $\Delta H_{\text{at}}^\ominus$ ) for elements
  - E.g. The standard enthalpy change of atomisation for sodium is the energy required to form 1 mole of **gaseous** sodium atoms:



### Worked Example

Write the equations for the standard enthalpy change of atomisation, ( $\Delta H_{\text{at}}^\ominus$ ) 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)
  - $\text{K}(\text{s}) \rightarrow \text{K}(\text{g})$

**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)
  - $\text{Hg}(\text{l}) \rightarrow \text{Hg}(\text{g})$



## 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



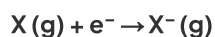
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# Electron Affinity

## 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



- $EA_1$  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 / $\text{kJ mol}^{-1}$	
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



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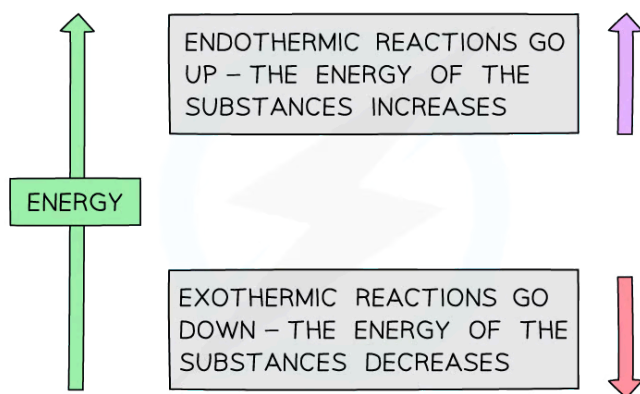
- Therefore, **more energy is released** when an electron is added to chlorine, making its first electron affinity (**EA<sub>1</sub>**) **more exothermic** than that of sulfur
- As you move down Group 16 or Group 17:
  - The **outermost electrons are farther from the nucleus**, so the attractive force 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



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

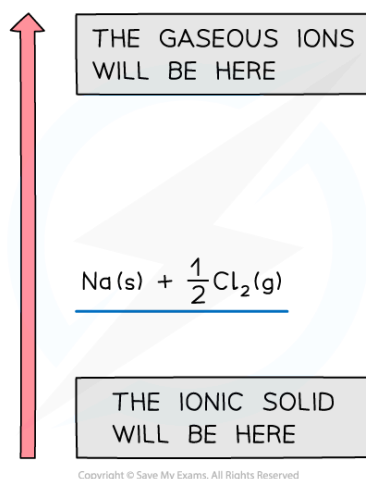
- The cycle shows all the steps needed to turn atoms into gaseous ions and from gaseous ions into the ionic lattice
- The alternative route to the ionic lattice begins from the enthalpy of formation of the elements in their standard states

## 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





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- 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



- The enthalpy of atomisation of chlorine is

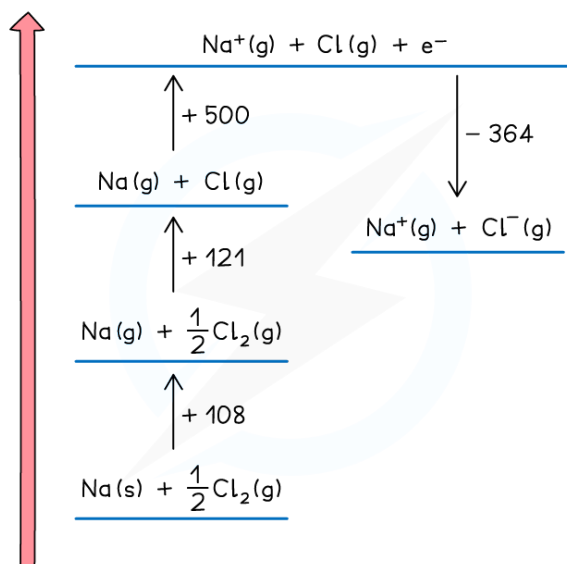


- We can show the products of the process on the horizontal lines and the energy value against a vertical arrow connecting the energy levels

## 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



- The change is endothermic so the direction continues upwards
- The chlorine atom gains an electron, so this is electron affinity

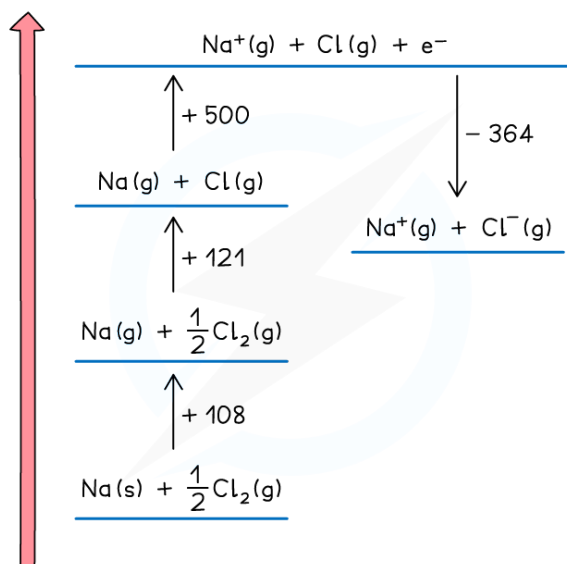


- The exothermic change means this is downwards
- The change is displaced to the right to make the diagram easier to read

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



Your notes

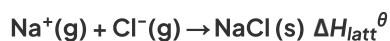


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- The two remaining parts of the cycle can now be completed
- The enthalpy of formation of sodium chloride is added at the bottom of the diagram



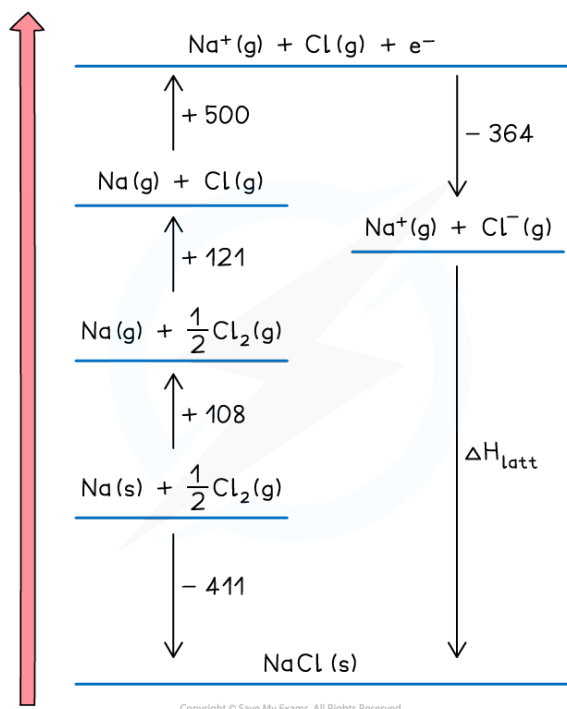
- This is an exothermic change for sodium chloride so the arrow points downwards
- Enthalpy of formation can be exothermic or endothermic, so you may need to show it above the elements (and displaced to the right) for an endothermic change
- The final change is lattice enthalpy, which is usually shown as a formation. For sodium chloride the equation is



## Drawing a Born-Haber cycle step 4 – completing the cycle



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- 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

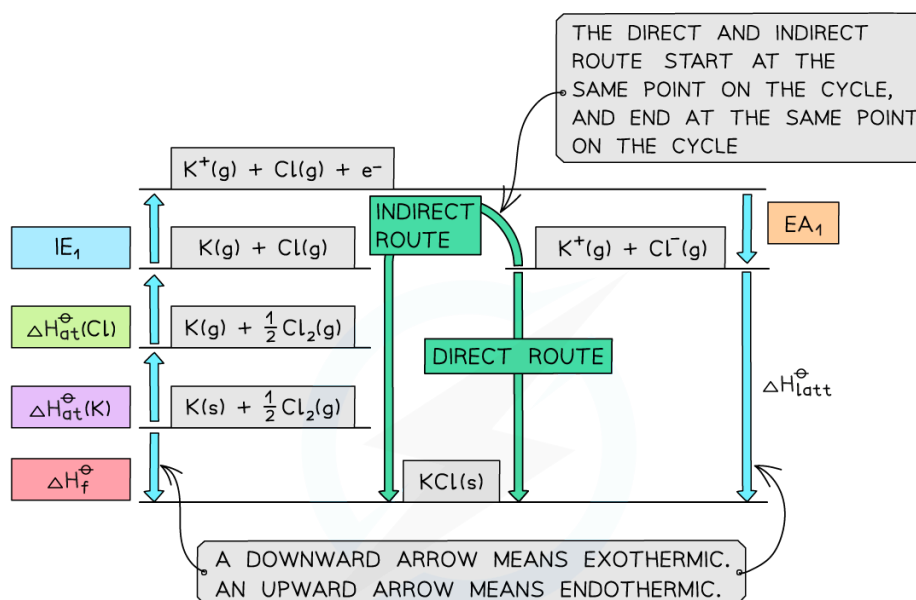
Construct a Born-Haber Cycle which can be used to calculate the lattice energy of potassium chloride.

Step	Equation	Enthalpy Change
Convert K(s) atoms into K(g) atoms	$\text{K(s)} \rightarrow \text{K(g)}$	$\Delta H_{\text{at}}^{\ominus}$
Convert K(g) atoms into $\text{K}^+(\text{g})$ ions	$\text{K(g)} \rightarrow \text{K}^+(\text{g})$	$IE_1$
Convert $\text{Cl}_2(\text{g})$ molecules into Cl(g) atoms	$\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$	$\Delta H_{\text{at}}^{\ominus}$
Convert Cl(g) atoms into $\text{Cl}^-(\text{g})$ ions	$\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$	$EA_1$
Add up all values to get $\Delta H_1^{\ominus}$		$\Delta H_1^{\ominus}$
Apply Hess's Law to find $\Delta H_{\text{latt}}^{\ominus}$		$\Delta H_{\text{latt}}^{\ominus}$

Answer:



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$$\Delta H_f^\ominus = \left( \Delta H_{at}^\ominus(K) \right) + \left( \Delta H_{at}^\ominus(Cl) \right) + \left( IE_1 \right) + \left( EA_1 \right) + \left( \Delta H_{latt}^\ominus \right)$$

$$\therefore \Delta H_{latt}^\ominus = \left( \Delta H_f^\ominus \right) - \underbrace{\left( EA_1 \right) - \left( IE_1 \right) - \left( \Delta H_{at}^\ominus(Cl) \right) - \left( \Delta H_{at}^\ominus(K) \right)}_{\Delta H_1^\ominus}$$

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### 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	$Mg(s) \rightarrow Mg(g)$	$\Delta H_{at}^\ominus$
Convert Mg (g) atoms into $Mg^+(g)$ ions	$Mg(g) \rightarrow Mg^+(g) + e^-(g)$	$IE_1$
Convert $Mg^+(g)$ atoms into $Mg^{2+}(g)$ ions	$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-(g)$	$IE_2$
Convert $O_2(g)$ molecules into O (g) atoms	$\frac{1}{2}O_2(g) \rightarrow O(g)$	$\Delta H_{at}^\ominus$
Convert O (g) atoms into $O^-(g)$ ions	$O(g) + e^- \rightarrow O^-(g)$	$EA_1$
Convert $O^-(g)$ atoms into $O^{2-}(g)$ ions	$O^-(g) + e^- \rightarrow O^{2-}(g)$	$EA_2$
Add up all values to get $\Delta H_1^\ominus$		$\Delta H_1^\ominus$

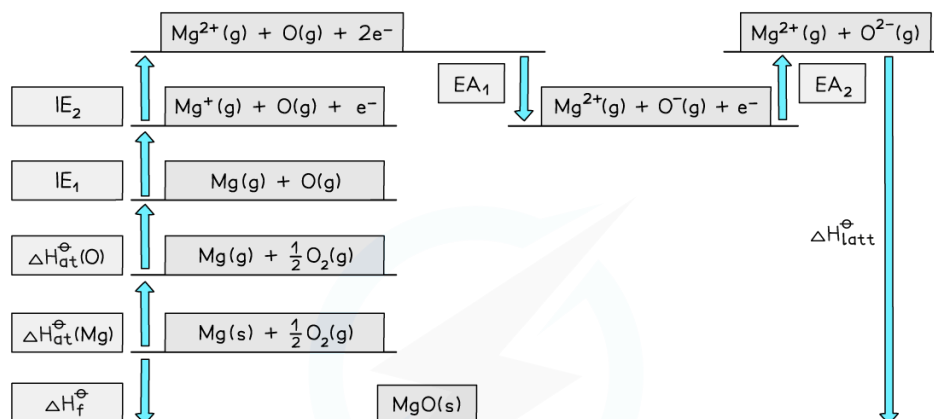
Apply Hess's Law to find  $\Delta H_{latt}^\ominus$

$\Delta H_{latt}^\ominus$



Your notes

Answer:



$$\Delta H_f^\ominus = \left( \Delta H_{at}^\ominus(\text{Mg}) \right) + \left( \Delta H_{at}^\ominus(\text{O}) \right) + \left( \text{IE}_1 \right) + \left( \text{IE}_2 \right) + \left( \text{EA}_1 \right) + \left( \text{EA}_2 \right) + \left( \Delta H_{latt}^\ominus \right)$$

$$\therefore \Delta H_{latt}^\ominus = \left( \Delta H_f^\ominus \right) - \underbrace{\left( \text{EA}_1 \right) - \left( \text{EA}_2 \right) - \left( \text{IE}_1 \right) - \left( \text{IE}_2 \right) - \left( \Delta H_{at}^\ominus(\text{Mg}) \right) - \left( \Delta H_{at}^\ominus(\text{O}) \right)}_{\Delta H_1^\ominus}$$

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# Calculations Using Born–Haber Cycles

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

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

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

- $\Delta H_{latt}^\ominus$
- $\Delta H_f^\ominus$
- $\Delta H_I^\ominus$  (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

$$\Delta H_f^\ominus = \Delta H_I^\ominus + \Delta H_{latt}^\ominus$$

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

$$\Delta H_{latt}^\ominus = \Delta H_f^\ominus - \Delta H_I^\ominus$$


- When calculating the  $\Delta H_{latt}^\ominus$ , 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  $\text{MgCl}_2$  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  $\text{Cl}^-$  ions



### Worked Example

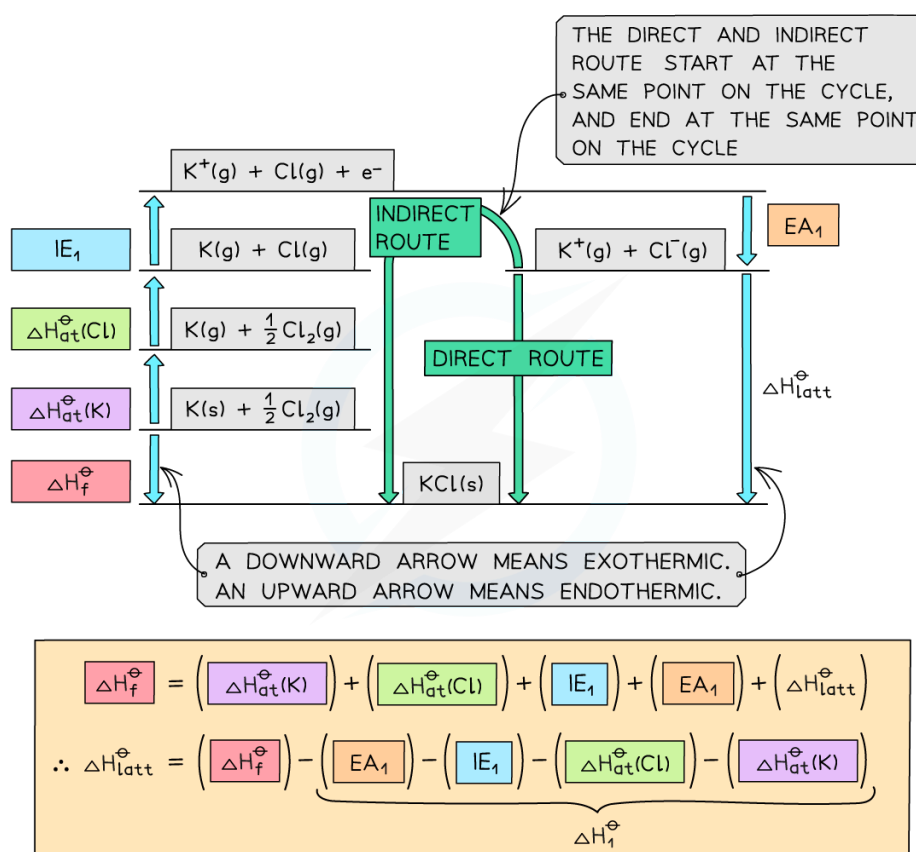
Using the data below, calculate the  $\Delta H_{\text{latt}}^\ominus$  of potassium chloride, KCl.

	$\Delta H_{\text{at}}^\ominus / \text{kJ mol}^{-1}$	IE / EA / $\text{kJ mol}^{-1}$
K	+90	+418
Cl	+122	-349
$\Delta H_f^\ominus / \text{kJ mol}^{-1}$		
KCl	-437	

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**Answer:**

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



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

- $\Delta H_{\text{latt}}^\ominus = \Delta H_f^\ominus - \Delta H_f^\ominus$
- $\Delta H_{\text{latt}}^\ominus = \Delta H_f^\ominus - [(\Delta H_{\text{at}}^\ominus \text{ K}) + (\Delta H_{\text{at}}^\ominus \text{ Cl}) + (\text{IE}_1 \text{ K}) + (\text{EA}_1 \text{ Cl})]$
- Step 3: Substitute in the numbers:
- $\Delta H_{\text{latt}}^\ominus = (-437) - [(+90) + (+122) + (+418) + (-349)] = -718 \text{ kJ mol}^{-1}$



## Worked Example

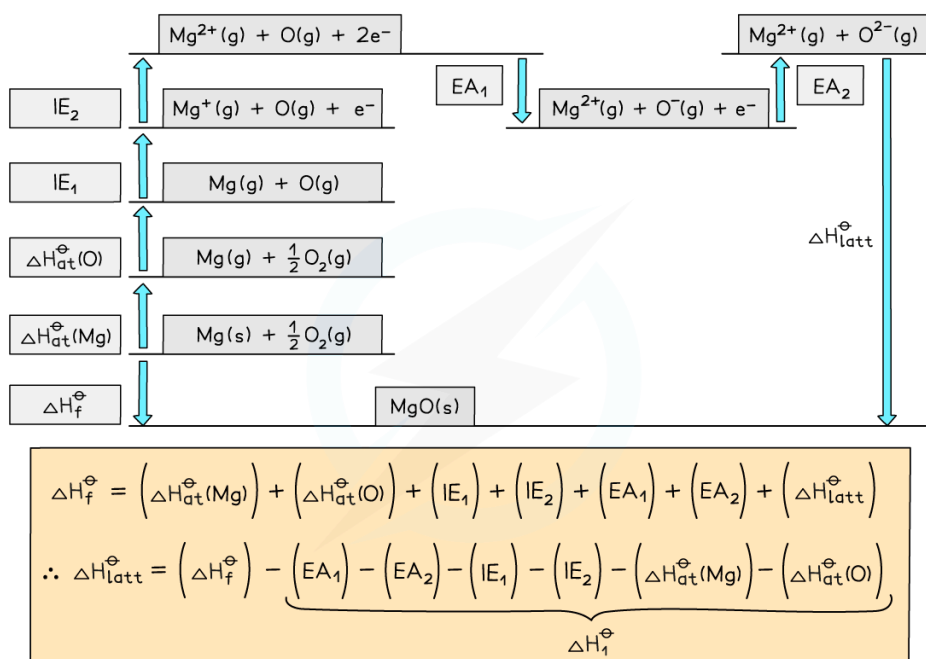


Using the data below, calculate the  $\Delta H_{latt}^\theta$  of magnesium oxide, MgO.

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

**Answer:**

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



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

- $\Delta H_{latt}^\theta = \Delta H_f^\theta - \Delta H_1^\theta$
- $\Delta H_{latt}^\theta = \Delta H_f^\theta - [(\Delta H_{at}^\theta \text{ Mg}) + (\Delta H_{at}^\theta \text{ O}) + (IE_1 \text{ Mg}) + (IE_2 \text{ Mg}) + (EA_1 \text{ O}) + (EA_2 \text{ O})]$
- 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!



Your notes



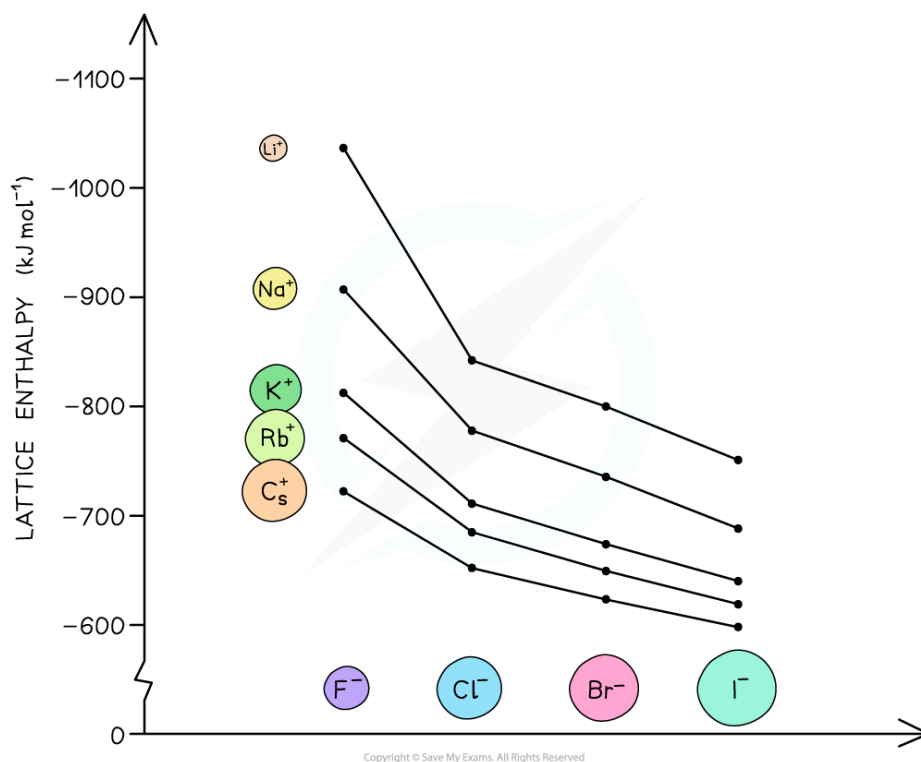
# Lattice Energy: Ionic Charge & Radius

- 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<sup>-</sup> ions
  - Cs<sup>+</sup> is larger than K<sup>+</sup>, 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  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  ions, while KCl contains  $\text{K}^{+}$  and  $\text{Cl}^{-}$  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,  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  ions are smaller than  $\text{K}^{+}$  and  $\text{Cl}^{-}$ , further increasing the exothermic value



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