Edexcel International A Level (IAL) Chemistry

Your notes

Energetics

Contents

- Born-Haber Cycles - Key Terms
- Born-Haber Cycles
- Polarisation
- Enthalpy of Solution - Key Terms
- Enthalpy of Solution - Calculations
- Enthalpy of Solution - Ionic Charge & Radius

Your notes

Born-Haber Cycles - Key Terms

Lattice energy

- As with bond enthalpy, **lattice energy** ($\Delta_{latt}H^{\ominus\ominus}$) can be expressed as a formation or dissociation process
- As a formation process, it is the enthalpy change when **1 mole** of an **ionic compound** is formed from its **gaseous ions** (under standard conditions)
- The $\Delta_{latt}H^{\ominus\ominus}$ is therefore **exothermic,** as when ions are **combined** to form an **ionic solid lattice** there is an extremely large release of energy
  - Since this is an exothermic process, the enthalpy change will 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 $\Delta_{latt}H^{\ominus\ominus}$ 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 $\Delta_{latt}H^{\ominus\ominus}$ of an ionic compound **cannot** be determined **directly** by one single experiment
- Multiple experimental values and an **energy cycle** are used to find the $\Delta_{latt}H^{\ominus\ominus}$ of ionic compounds
- The lattice energy ($\Delta_{latt}H^{\ominus\ominus}$) of an ionic compound can be written as an equation
  - For example, sodium chloride is an ionic compound formed from sodium (Na^+) and chloride (Cl^-) ions
  - Since the lattice energy is the enthalpy change when 1 mole of sodium chloride is formed from gaseous sodium and chloride ions, the equation for this process is:

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \quad \Delta_{latt}H^{\ominus\ominus} = -776\ kJ\ mol^{-1}$$

Worked Example

Writing equations for lattice energy

Write down the equations which represent the lattice energy of:

(i) Magnesium oxide

(ii) Lithium chloride

Answer

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** ($\Delta_{at}H^{\ominus\ominus}$) is the **enthalpy change** when **1 mole of gaseous atoms** is formed from its **element** under standard conditions
- The $\Delta_{at}H^{\ominus\ominus}$ is always **endothermic** as energy is always required to **break** any bonds between the atoms in the element, to break 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 ($\Delta_{at}H^{\ominus\ominus}$) for elements
- For example, sodium in its elemental form is a **solid**
- The standard enthalpy change of atomisation for sodium is the energy required to form 1 mole of **gaseous** sodium atoms:

$$Na(s) \rightarrow Na(g) \qquad \Delta_{at}H^{\ominus\ominus} = +108\ kJ\ mol^{-1}$$

Worked Example

Writing equations for the standard enthalpy change of atomisation

Write down the equations for the standard enthalpy change of atomisation ($\Delta_{at}H^{\ominus\ominus}$) for:

(i) Potassium

(ii) Mercury

Answer

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:

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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)

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

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Electron Affinity

- The **electron affinity** ($\Delta_{ea}H$) of an element is the energy change when **one mole** of electrons is gained by **one mole** of gaseous atoms of an element to form **one mole** of gaseous ions under standard conditions
- For example, the first electron affinity of chlorine is:

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta_{ea}H^{\ominus} = -364\ kJ\ mol^{-1}$$

- The **first electron affinity** is always **exothermic** as energy is released when electrons are attracted to the atoms
- However, the **second electron affinity** of an element can be **endothermic** as illustrated by oxygen:

$$O^-(g) + e^- \rightarrow O^{2-}(g) \qquad \Delta_{ea}H^{\ominus} = +844\ kJ\ mol^{-1}$$

- This is because a large force of **repulsion** must be overcome between the negatively charged ion and the second electron requiring a large input of energy

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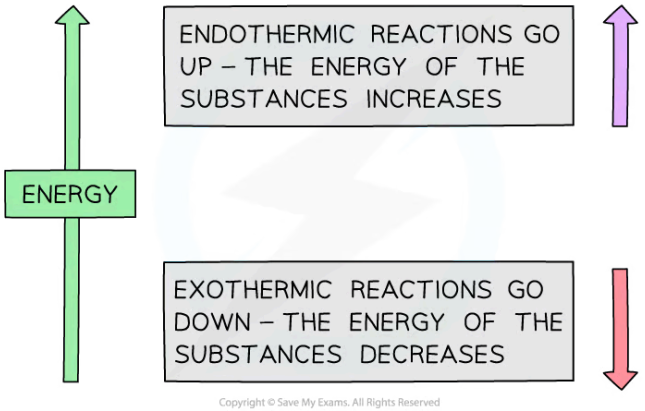
Born-Haber Cycles - Construction

- A **Born-Haber cycle** is a specific application of Hess' 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

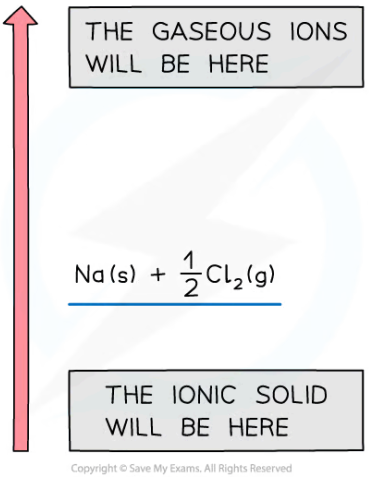


The basic principle of a Born-Haber cycle

- 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

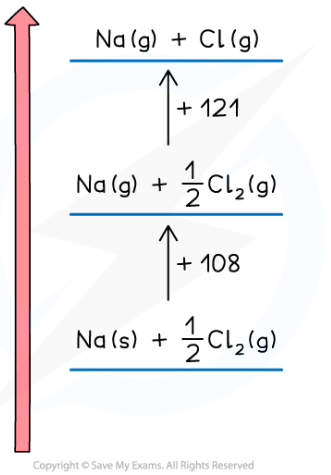
- Next, we need to create the gaseous ions
- This is a two step process of first creating the gaseous atoms and then turning them into ions
- Creating gaseous atoms is a bond breaking process, so arrows must be drawn upwards
- It doesn't matter whether you start with sodium or chlorine
- The enthalpy of atomisation of sodium is

$$Na\,(s) \rightarrow Na\,(g) \qquad \Delta_{at}H^{\ominus} = +108\ kJ\ mol^{-1}$$

- The enthalpy of atomisation of chlorine is

$$\tfrac{1}{2}Cl_2\,(g) \rightarrow Cl\,(g) \qquad \Delta_{at}H^{\ominus} = +121\ kJ\ mol^{-1}$$

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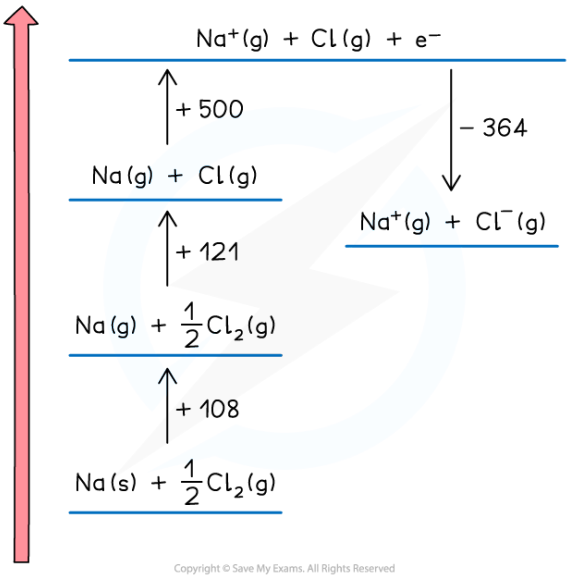
- Now the ions are created
- The sodium ion loses an electron, so this energy change is the first ionisation energy for sodium

$$Na\,(g) \rightarrow Na^{+}\,(g) + e^{-} \qquad \Delta_{ie}H^{\ominus} = +500\ kJ\ mol^{-1}$$

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

$$Cl\,(g) + e^{-} \rightarrow Cl^{-}\,(g) \qquad \Delta_{ea}H^{\ominus} = -364\ kJ\ mol^{-1}$$

- 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

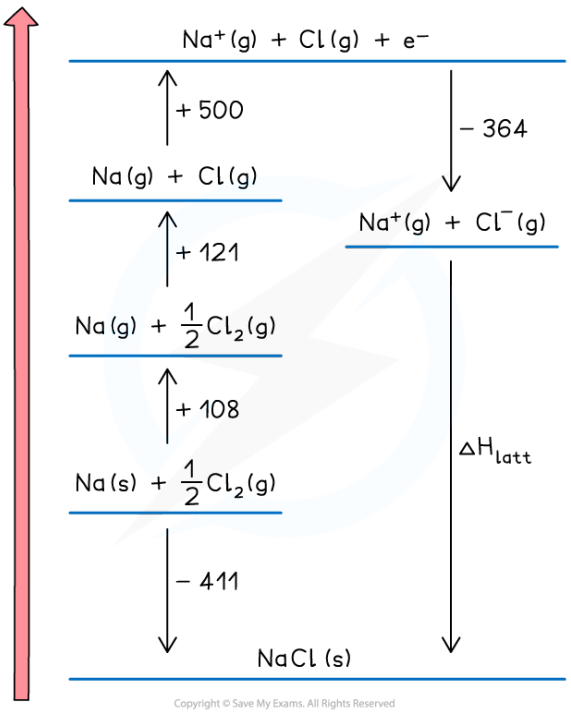
- The two remaining parts of the cycle can now be completed
- The enthalpy of formation of sodium chloride is added at the bottom of the diagram

$$Na\,(s) + \tfrac{1}{2}Cl_2\,(g) \rightarrow NaCl\,(s) \qquad \Delta_{f}H^{\ominus} = -411\ kJ\ mol^{-1}$$

- 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

$$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl\,(s)\ \Delta_{latt}H^{\ominus}$$

Your notes



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

Constructing a Born-Haber cycle for KCl

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

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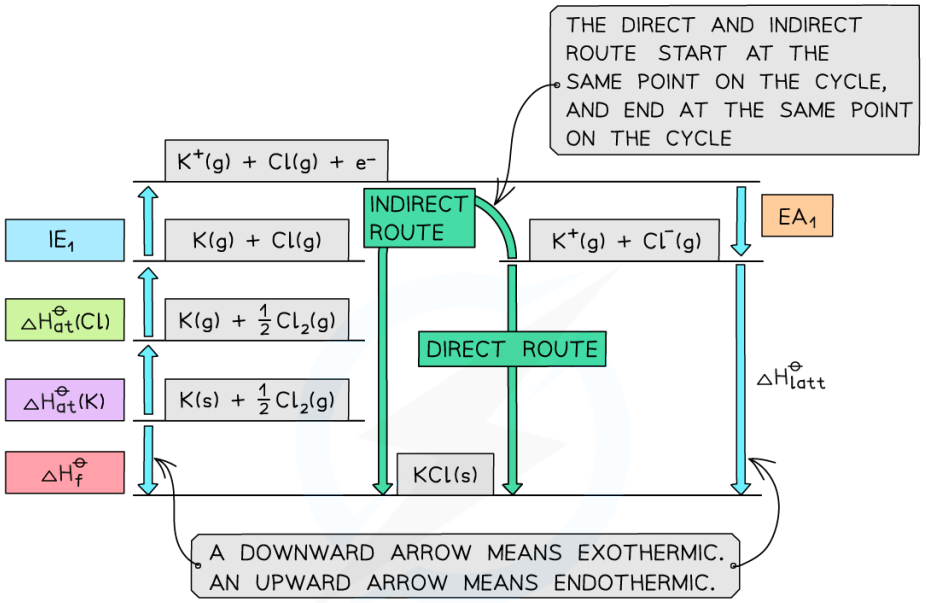
Step	Equation	Enthalpy Change
Convert K(s) atoms into K(g) atoms	$K(s) \longrightarrow K(g)$	$\Delta H^{\ominus}_{at}$
Convert K(g) atoms into $K^+(g)$ ions	$K(g) \longrightarrow K^+(g) + e^-$	IE_1
Convert $Cl_2(g)$ molecules into Cl(g) atoms	$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	$\Delta H^{\ominus}_{at}$
Convert Cl(g) atoms into $Cl^-(g)$ ions	$Cl(g) + e^- \longrightarrow Cl^-(g)$	EA_1
Add up all values to get $\Delta H^{\ominus}_1$		$\Delta H^{\ominus}_1$
Apply Hess's Law to find $\Delta H^{\ominus}_{latt}$		$\Delta H^{\ominus}_{latt}$

Answer



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

$$\therefore \Delta H^{\ominus}_{latt} = \left(\Delta H^{\ominus}_f\right) - \underbrace{\left(EA_1\right) - \left(IE_1\right) - \left(\Delta H^{\ominus}_{at}(Cl)\right) - \left(\Delta H^{\ominus}_{at}(K)\right)}_{\Delta H^{\ominus}_1}$$

Worked Example

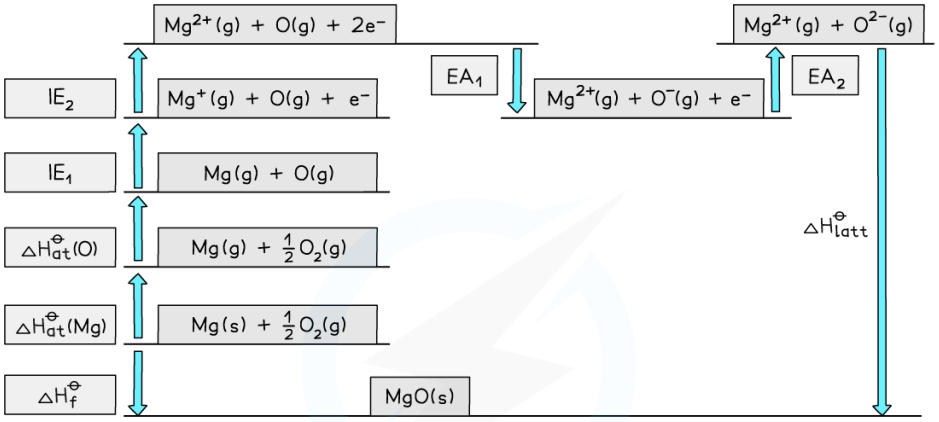
Constructing a Born-Haber cycle for MgO

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	$Mg(s) \longrightarrow Mg(g)$	$\Delta H^{\ominus}_{at}$
Convert Mg(g) atoms into $Mg^+(g)$ ions	$Mg(g) \longrightarrow Mg^+(g) + e^-$	IE_1
Convert $Mg^+(g)$ ions into $Mg^{2+}(g)$ ions	$Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-$	IE_2
Convert $O_2(g)$ molecules into O(g) atoms	$\frac{1}{2}O_2(g) \longrightarrow O(g)$	$\Delta H^{\ominus}_{at}$
Convert O(g) atoms into $O^-(g)$ ions	$O(g) + e^- \longrightarrow O^-(g)$	EA_1
Convert $O^-(g)$ ions into $O^{2-}(g)$ ions	$O^-(g) + e^- \longrightarrow O^{2-}(g)$	EA_2
Add up all values to get $\Delta H^{\ominus}_1$		$\Delta H^{\ominus}_1$
Apply Hess's Law to find $\Delta H^{\ominus}_{latt}$		$\Delta H^{\ominus}_{latt}$

Answer

Your notes



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

$$\therefore \Delta H^{\ominus}_{latt} = \left(\Delta H^{\ominus}_{f}\right) - \underbrace{\left(EA_1\right) - \left(EA_2\right) - \left(IE_1\right) - \left(IE_2\right) - \left(\Delta H^{\ominus}_{at}(Mg)\right) - \left(\Delta H^{\ominus}_{at}(O)\right)}_{\Delta H^{\ominus}_{1}}$$

Your notes

Born-Haber Cycles – Calculations

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

$$\Delta_f H^{\ominus\ominus} = \Delta_{at} H^{\ominus\ominus} + \Delta_{at} H^{\ominus\ominus} + IE + EA + \Delta_{latt} H^{\ominus\ominus}$$

- If we simplify this into three terms, this makes the equation easier to see:
  - $\Delta H_{latt}^{\ominus\ominus}$
  - $\Delta H_{f}^{\ominus\ominus}$
  - $\Delta H_{1}^{\ominus\ominus}$ (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

$$\Delta_f H^{\ominus\ominus} = \Delta_1 H^{\ominus\ominus} + \Delta_{latt} H^{\ominus\ominus}$$

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

$$\Delta_{latt} H^{\ominus\ominus} = \Delta_f H^{\ominus\ominus} - \Delta_1 H^{\ominus\ominus}$$

- When calculating the $\Delta H_{latt}^{\ominus\ominus}$, 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 $MgCl_2$ 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

Your notes

Worked Example

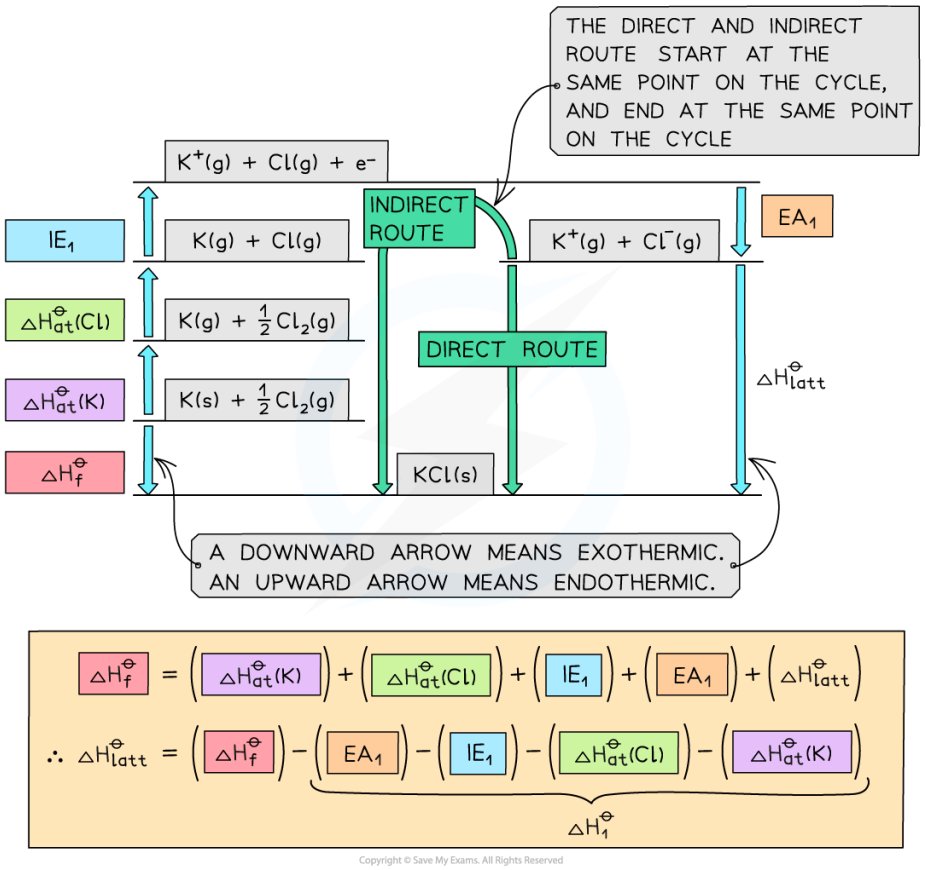
Calculating the lattice energy of KCl

Given the data below, calculate the $\Delta_{latt}H^{\ominus}$ of potassium chloride (KCl)

	$\Delta H_{at}^{\ominus}$ (kJ mol^{-1})	IE/EA (kJ mol^{-1})
K	+90	+418
Cl	+122	−349
$\Delta H_f^{\ominus}$ (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:

$$\Delta_{latt}H^{\ominus} = \Delta_f H^{\ominus} - \Delta_1 H^{\ominus}$$

$$\Delta_{latt}H^{\ominus} = \Delta_f H^{\ominus} - [(\Delta_{at}H^{\ominus}\,K) + (\Delta_{at}H^{\ominus}\,Cl) + (IE_1\,K) + (EA_1\,Cl)]$$

Step 3: Substitute in the numbers:

$$\Delta_{latt}H = (-437) - [(+90) + (+122) + (+418) + (-349)] = -718\ kJ\ mol^{-1}$$

Worked Example

Calculating the lattice energy of MgO

Given the data below, calculate the of $\Delta_{latt}H^{\ominus}$ magnesium oxide of magnesium oxide (MgO)

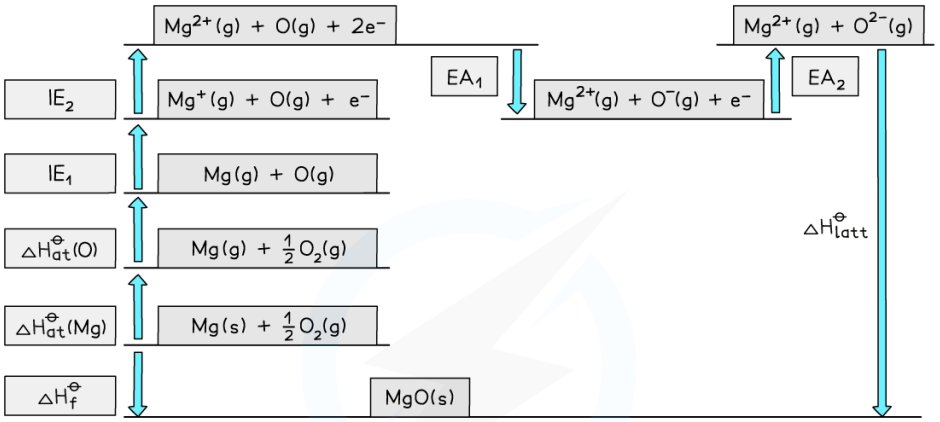
Your notes

Your notes

	$\Delta H_{at}^{\ominus}$ (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
$\Delta H_f^{\ominus}$ (kJ mol^{-1})			
MgO	−602		

Answer

Step 1: The corresponding Born-Haber cycle is:



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

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

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

$$\Delta_{latt}H^{\ominus} = \Delta_f H^{\ominus} - \Delta_1 H^{\ominus}$$

$$\Delta_{latt}H^{\ominus} = \Delta_f H^{\ominus} - [(\Delta_{at}H^{\ominus}\,Mg) + (\Delta_{at}H^{\ominus}\,O) + (IE_1\,Mg) + (IE_2\,Mg) + (EA_1\,O) + (EA_2\,O)]$$

Step 3: Substitute in the numbers:

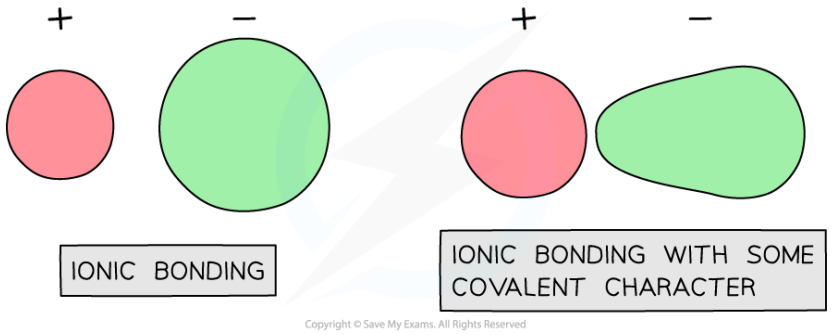
$$\Delta_{latt}H^{\ominus} = (-602) - [(+148) + (+248) + (+736) + (+1450) + (-142) + (+770)]$$

$$= -3812\ kJ\ mol^{-1}$$

Your notes

Polarisation

- Theoretical lattice energies assume a perfect ionic model where the ions are 100% spherical and the attractions are purely electrostatic
  - So overall, there has a been a complete and irreversible exchange of outer shell electrons between the two elements in the compound so that one ion is negatively charged and the other ion positively charged and the charges are whole values
- Theoretical lattice energy can differ from measured lattice energy
- This is because covalent character is introduced when there is **polarisation** of the anions
- When this occurs, the cation attracts electrons from the anion therefore distorting electron density of the anion leading to a degree of **covalent character**



Polarisation of anion leading to covalent character

Cations

- A cation with a large charge density will have a larger **polarising power**
- The charge density can be calculated as the charge of the cation divided but the surface area, for example
  - K^+ will have a lower polarising power than Li^+ as the ionic radius is greater
  - Na^+ will have a lower polarising power than Mg^{2+} as the charge is smaller
- So a cation that is small and highly charged will have the greatest polarising power

Anions

- Anions are polarised
- The polarisability of the anion depends of its ionic radius
- The larger the ionic radius the more easily it will be distorted, for example
  - Br- will be more polarisable than Cl^- as the ionic radius is larger

- A rough approximation of the charge density can be determines by dividing the charge by the square of its ionic radius and this can help us estimate the extent of covalent character

$$\text{charge density} \sim \frac{\text{charge}}{r^2}$$

Comparing the Covalent Character of NaCl and $MgCl_2$

	NaCl	$MgCl_2$
Charge density of cation	$\frac{1}{(0.095)^2} = 111$	$\frac{2}{(0.060)^2} = 556$
Experimental lattice energy ($kJ\ mol^{-1}$)	−780	−2526
Theoretical lattice energy ($kJ\ mol^{-1}$)	−770	−2326
Potential difference	1.28	7.92
Extent of covalent character	very little	more than NaCl

Your notes

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Enthalpy of Solution – Key Terms

Enthalpy of solution

- The **standard enthalpy change of solution ($\Delta_{sol}H$)** is the enthalpy change when **1 mole** of an ionic substance **dissolves** in sufficient water to form an **infinitely dilute solution**
- The symbol **(aq)** is used to show that the solid is dissolved in **sufficient water**
  - For example, the enthalpy changes of solution for potassium chloride are described by the following equations:

$$KCl\,(s) + aq \rightarrow KCl\,(aq)$$

OR

$$KCl\,(s) + aq \rightarrow K^+\,(aq) + Cl^-\,(aq)$$

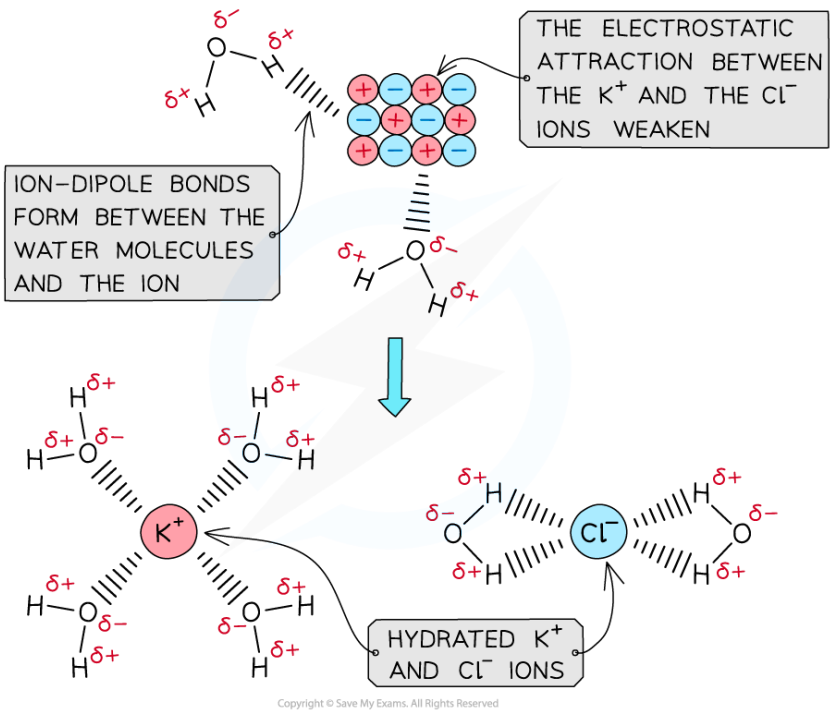
- $\Delta_{sol}H^{\ominus}$ can be **exothermic** (negative) or **endothermic** (positive)

Enthalpy of hydration

- The **standard enthalpy change of hydration ($\Delta_{hyd}H$)** is the enthalpy change when **1 mole** of a specified **gaseous ion dissolves** in sufficient water to form an infinitely dilute **solution**
  - For example, the enthalpy change of hydration for magnesium ions is described by the following equation:

$$Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$$

- Hydration enthalpies are the measure of the energy that is released when there is an attraction formed between the ions and water molecules
  - Hydration enthalpies are **exothermic**
- When an **ionic solid** dissolves in water, positive and negative ions are formed
- Water is a **polar** molecule with a δ- oxygen (O) atom and δ+ hydrogen (H) atoms which will form **ion–dipole attractions** with the ions present in the solution
- The oxygen atom in water will be attracted to the **positive ions** and the hydrogen atoms will be attracted to the **negative ions**



The polar water molecules will form ion-dipole bonds with the ions in solution causing the ions to become hydrated

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Enthalpy of Solution – Calculations

- Questions in this topic typically ask you to calculate the hydration enthalpy of one of the ions, given the lattice enthalpy, enthalpy of solution and hydration enthalpy of the other ion.
- This can be done by constructing an appropriate energy cycle and using Hess's Law to find the unknown energy value
- The energy cycle above shows that there are two routes to go from the gaseous ions to the ions in an aqueous solution:
  - **Route 1**: going from gaseous ions → ionic solid → ions in aqueous solution (this is the **indirect route**)
    - **Route 2**: going from gaseous ions → ions in aqueous solution (this is the **direct route**)
- According to **Hess's law,** the enthalpy change for both routes is the same, such that:

$$\Delta_{hyd}H^{\ominus\ominus} = \Delta_{latt}H^{\ominus\ominus} + \Delta_{sol}H^{\ominus\ominus}$$

- Each ion will have its own enthalpy change of hydration, $\Delta H_{hyd}^{\ominus\ominus}$, which will need to be taken into account during calculations
  - The total $\Delta_{hyd}H^{\ominus\ominus}$ is found by adding the $\Delta_{hyd}H^{\ominus\ominus}$ values of both anions and cations together

Worked Example

Constructing an energy cycle for KCl

Calculate the enthalpy of hydration of the chloride ion given the following data:

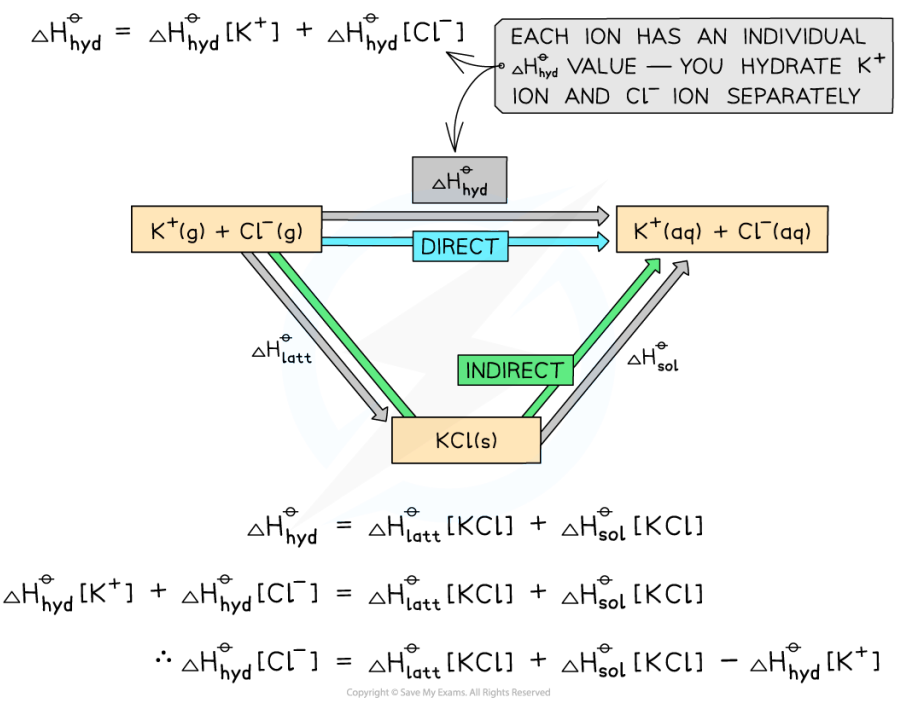
$\Delta_{latt}H^{\ominus\ominus}$ [KCl] = -711 kJ mol^{-1}

$\Delta_{sol}H^{\ominus\ominus}$ [KCl] = +26 kJ mol^{-1}

$\Delta_{hyd}H^{\ominus\ominus}$ [K^+] = -322 kJ mol^{-1}

Answer

Step 1: Draw the energy cycle and make $\Delta_{hyd}H$[Cl^-] the subject of the formula:



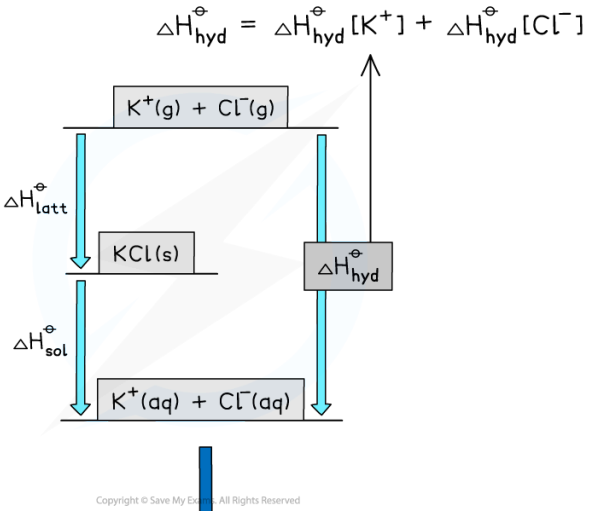
Step 2: Substitute the values to find $\Delta_{hyd}H[Cl^-]$

$$\Delta_{hyd}H[Cl^-] = (-711) + (+26) - (-322) = -363 \text{ kJ mol}^{-1}$$

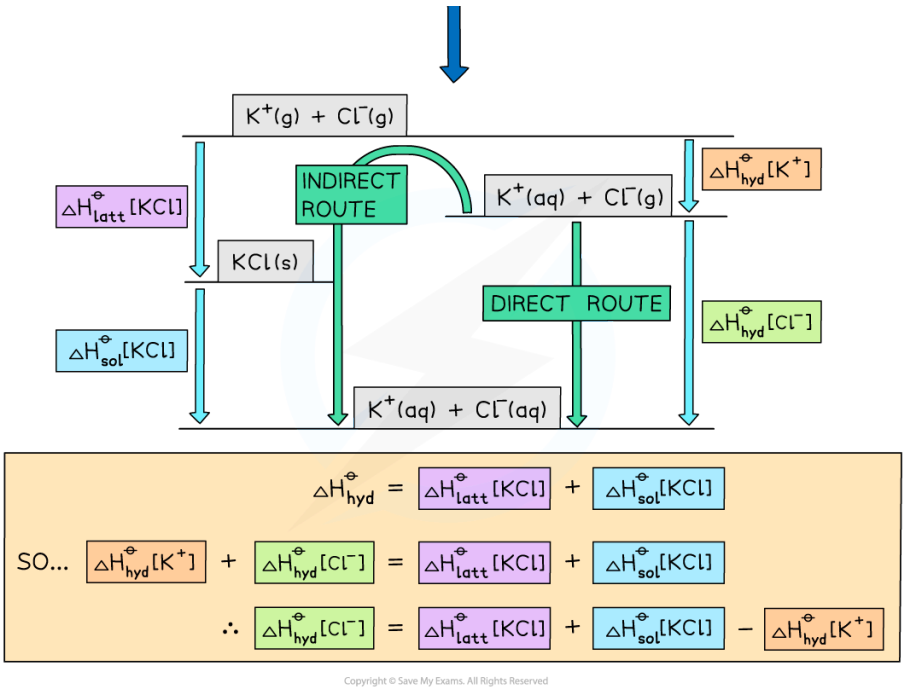
Alternative Diagram

- You can also draw a Born-Haber cycle as an alternative approach to the same problem

Energy level diagram:



Your notes



Your notes

Worked Example

Constructing an energy cycle and energy level diagram of $MgCl_2$

Construct an energy cycle to calculate the $\Delta_{hyd}H^{\ominus}$ of magnesium ions in magnesium chloride, given the following data:

$\Delta_{latt}H\,[MgCl_2] = -2592\ kJ\ mol^{-1}$

$\Delta_{sol}H\,[MgCl_2] = -55\ kJ\ mol^{-1}$

$\Delta_{hyd}H\,[Cl^-] = -363\ kJ\ mol^{-1}$

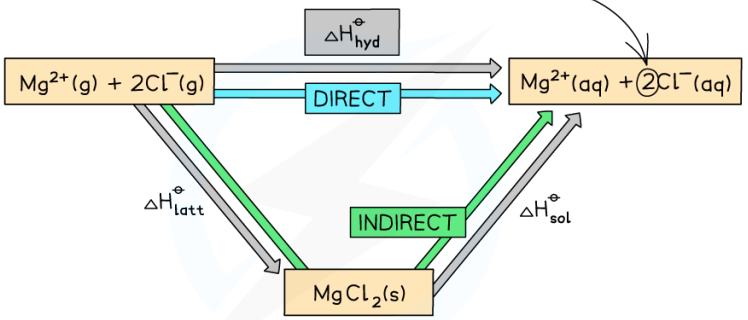
Answer

Step 1: Draw an energy cycle:

Your notes

$$\Delta H^{\ominus}_{hyd} = \Delta H^{\ominus}_{hyd}[Mg^{2+}] + 2\Delta H^{\ominus}_{hyd}[Cl^-]$$

SINCE THERE ARE 2 MOLES OF Cl^-, THE HYDRATION ENTHALPY ($\Delta H^{\ominus}_{hyd}$) WILL BE DOUBLE



$$\Delta H^{\ominus}_{hyd} = \Delta H^{\ominus}_{latt}[MgCl_2] + \Delta H^{\ominus}_{sol}[MgCl_2]$$

$$\Delta H^{\ominus}_{hyd}[Mg^{2+}] + 2\Delta H^{\ominus}_{hyd}[Cl^-] = \Delta H^{\ominus}_{latt}[MgCl_2] + \Delta H^{\ominus}_{sol}[MgCl_2]$$

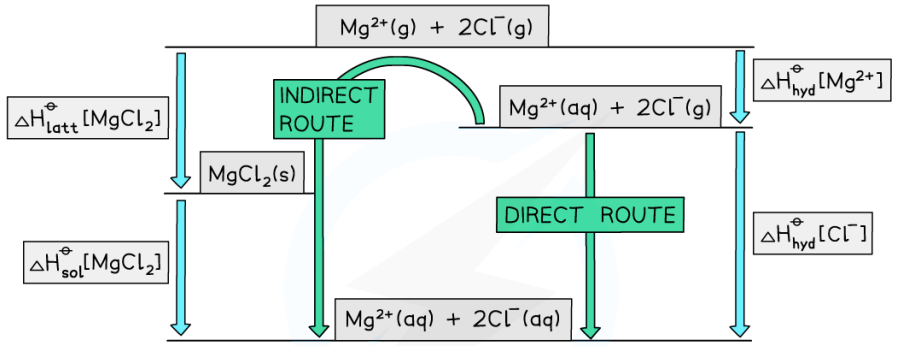
$$\therefore \Delta H^{\ominus}_{hyd}[Mg^{2+}] = \Delta H^{\ominus}_{latt}[MgCl_2] + \Delta H^{\ominus}_{sol}[MgCl_2] - 2\Delta H^{\ominus}_{hyd}[Cl^-]$$

Step 2: Substitute the values to find $\Delta H_{hyd}^{\ominus}[Mg^{2+}]$

$$\Delta H_{hyd}^{\ominus}[Mg^{2+}] = (-2592) + (-55) - (2 \times -363) = -1921 \text{ kJ mol}^{-1}$$

Alternative route to find $\Delta_{hyd}H^{\ominus}[Mg^{2+}]$

- Here is the same solution using a Born-Haber cycle



$$\Delta H^{\ominus}_{hyd} = \Delta H^{\ominus}_{latt}[MgCl_2] + \Delta H^{\ominus}_{sol}[MgCl_2]$$

$$\Delta H^{\ominus}_{hyd}[Mg^{2+}] + 2\Delta H^{\ominus}_{hyd}[Cl^-] = \Delta H^{\ominus}_{latt}[MgCl_2] + \Delta H^{\ominus}_{sol}[MgCl_2]$$

$$\Delta H^{\ominus}_{hyd}[Mg^{2+}] = \Delta H^{\ominus}_{latt}[MgCl_2] + \Delta H^{\ominus}_{sol}[MgCl_2] - 2\Delta H^{\ominus}_{hyd}[Cl^-]$$

Examiner Tips and Tricks

It doesn't matter whether you use Hess cycles or Born-Haber style cycles to solve these problems as long as the information is correctly labelled and the direction of

the arrows matches the definitions.Exam problems in this topic often show diagrams with missing labels which you have to complete and find unknown values.The key to success in energy cycle calculations is not to panic, but have a careful step-by-step approach, show your workings and use brackets to separate mathematical operations from the enthalpy changes.

Your notes

Enthalpy of Solution – Predictions

- When an ionic compound dissolves in water, there are two changes that need to take place
  - The lattice structure needs to be broken down and the ions must become hydrated
- The breaking down of the lattice structure is endothermic (equivalent to the reverse lattice energy) it also results in an increased number of moles of particles present, therefore entropy will increase
- The hydration of the ions is an exothermic process but results in water molecules becoming more ordered as they arrange themselves around the cations and anions
- This increasing in order decreases the entropy of the water
- Therefore to explain why some ionic compounds are soluble and some are insoluble we must consider both entropy and enthalpy changes involved
- As we have seen previously

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

And since

$$\Delta S_{surroundings} = -\frac{\Delta_{sol}H}{T}$$

The expression can become

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta_{sol}H}{T}$$

- Therefore the solubility of an ionic solid depends upon three factors
  - The **entropy of the system**, ΔS_{system}
  - The **enthalpy change of solution**, $\Delta_{sol}H$
  - The **temperature, in K, of the water**, T

If we consider ammonium nitrate, NH_4NO_3 (s), at 298 K

$$\mathbf{NH_4NO_3\,(s) \rightarrow NH_4^+\,(aq) + NO_3^-\,(aq)}$$

- The enthalpy change of solution, $\Delta_{sol}H = +25.8\ kJ\ mol^{-1}$
- The temperature, in K, of the water, $T = 298$ K

$$\Delta S_{system} = S[NH_4^+\,(aq)] + S[NO_3^-\,(aq)] - S[NH_4NO_3\,(s)]$$

$$= +113.4 + 146.4 - 151.1$$

$$= +108.7\ J\ K^{-1}\ mol^{-1}$$

$$\Delta S_{surroundings} = -\frac{\Delta_{sol}H}{T}$$

$$= -\frac{+25800}{298}$$

$$= -86.6\ J\ K^{-1}\ mol^{-1}$$

- Therefore the total entropy is:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= +108.7 + (-86.6)$$

$$= +22.1\ J\ K^{-1}\ mol^{-1}$$

- If the entropy change is positive, as it is for dissolving ammonium nitrate in water at 298 K, then this is thermodynamically spontaneous
- The activation energy (E_a) for this reaction is very low, we can conclude that at 298 K, ammonium nitrate is soluble in water

Your notes


Your notes

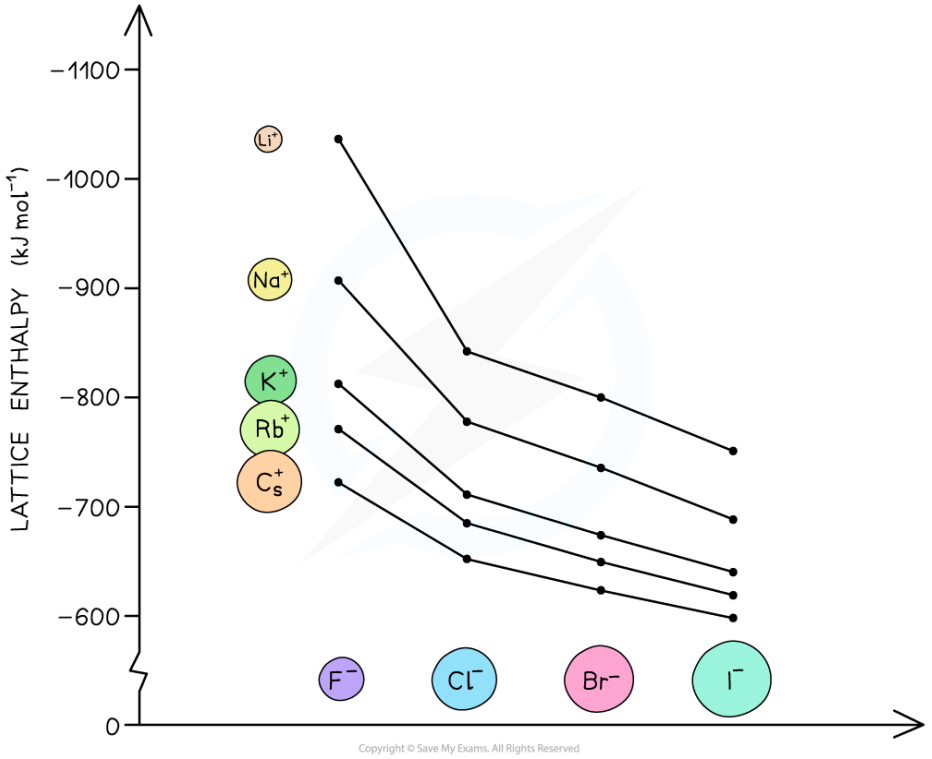
Enthalpy of Solution – Ionic Charge & Radius

Factors affecting lattice enthalpy

- 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** as the **ionic radius** of the ions **increases**
- This is because the charge on the ions is more **spread out** over the ion when the ions are **larger**
- The ions are also **further apart** from each other in the lattice
  - The attraction between ions is between the centres of the ions involved, so the bigger the ions the bigger the distance between the centre of the ions
- Therefore, the **electrostatic forces of attraction** between the oppositely charged ions in the lattice are **weaker**
- For example, the lattice energy of caesium fluoride (CsF) is **less exothermic** than the lattice energy of potassium fluoride (KF)
  - Since both compounds contain a fluoride (F^-) ion, the difference in lattice energy must be due to the caesium (Cs^+) ion in CsF and potassium (K^+) ion in KF
  - Potassium is a Group 1 and Period 4 element
  - Caesium is a Group 1 and Period 6 element
  - This means that the Cs^+ ion is **larger** than the K^+ ion
  - There are **weaker** electrostatic forces of attraction between the Cs^+ and F^- ions compared to K^+ and F^- ions
  - As a result, the **lattice energy** of CsF is **less exothermic** than that of KF



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

Ionic charge

- The lattice energy gets **more exothermic** as the **ionic charge** of the ions **increases**
- The greater the ionic charge, the **higher the charge density**
- This results in **stronger electrostatic attraction** between the oppositely charged ions in the lattice
- As a result, the lattice energy is **more exothermic**
- For example, the lattice energy of calcium oxide (CaO) is **more exothermic** than the lattice energy of potassium chloride (KCl)
  - Calcium oxide is an ionic compound which consists of calcium (Ca^{2+}) and oxide (O^{2-}) ions
  - Potassium chloride is formed from potassium (K^+) and chloride (Cl^-) ions
  - The ions in calcium oxide have a **greater ionic charge** than the ions in potassium chloride
  - This means that the electrostatic forces of attraction are **stronger** between the $Ca^{2+}$and O^{2-} compared to the forces between K^+ and Cl^-
  - Therefore, the lattice energy of calcium oxide is **more exothermic,** as more energy is released upon its formation from its gaseous ions

Your notes

- Ca^{2+} and O^{2-} are also smaller ions than K^{+} and Cl^{-}, so this also adds to the value for the lattice energy being more exothermic

Your notes

Factors affecting enthalpy of hydration

- Hydration enthalpies are exothermic as energy is given out as water molecules bond to the metal ions
- The negative ions are attracted to the **δ+ hydrogens** on the **polar water molecules** and the positive ions are attracted to the **δ− oxygen** on the polar water molecules
- The higher the charge density the greater the hydration enthalpy (e.g. smaller ions or ions with larger charges) as the ions attract the water molecules more strongly, for example:
- Fluoride ions, F^{-}, have more negative hydration enthalpies than chloride ions, Cl^{-}
- Magnesium ions, Mg^{2+}, have a more negative hydration enthalpy than barium ion, Ba^{2+}