Cambridge (CIE) A Level Chemistry

Your notes

Enthalpies of Solution & Hydration

Contents

Your notes

Enthalpy Change of Hydration & Solution

Enthalpy change of solution

- The **standard enthalpy change of solution (ΔH_{sol}^{θ})** is the enthalpy change when **1 mole** of an ionic substance **dissolves** in sufficient water to form a **very dilute solution** under standard conditions
- 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

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

- ΔH_{sol}^{θ} can be **exothermic** (negative) or **endothermic** (positive)

Enthalpy change of hydration

- The lattice energy (**ΔH_{latt}^{θ}**) of KCl is -711 kJ mol^{-1}
  - This means that 711 kJ mol^{-1} is **released** when the KCl ionic lattice is **formed**
  - Therefore, to **break** the attractive forces between the K^+ and Cl^- ions, +711 kJ mol^{-1} is needed
- However, the **ΔH_{sol}^{θ}** of KCl is +26 kJ mol^{-1}
- This means that another +685 kJ mol^{-1} (711 - 26) is required to break the KCl lattice
- This is **compensated** for by the **standard enthalpy change of hydration** (**ΔH_{hyd}^{θ}**)
  - The **standard enthalpy change of hydration (ΔH_{hyd}^{θ})** is the enthalpy change when **1 mole** of a specified **gaseous ion dissolves** in sufficient water to form a very dilute **solution** under standard conditions

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

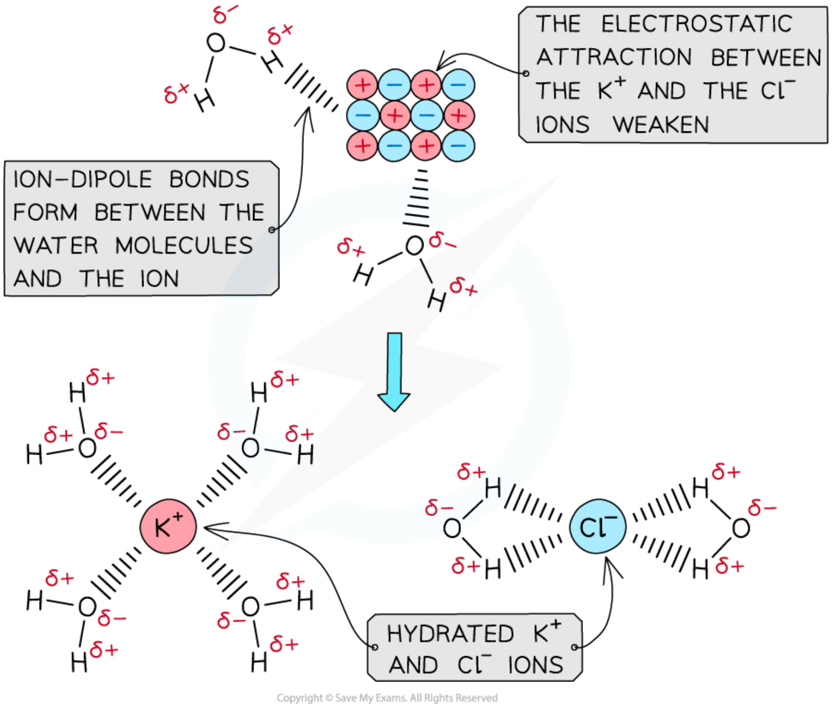
- Hydration enthalpies are the measure of the energy that is released when there is an attraction formed between the ions and water molecules
  - Hydration enthalpies are **exothermic**

Ion–Dipole interactions during dissolution

- When an **ionic solid dissolves in water**, it breaks into **positive and negative ions**
- Water is a **polar molecule**, with a δ^- oxygen atom and δ^+ hydrogen atoms

- The **oxygen atom** is attracted to **positive ions (cations)**
- The **hydrogen atoms** are attracted to **negative ions (anions)**
- These attractions form **ion-dipole bonds** between the water molecules and the ions

Interactions of polar water molecules and other ions in solution



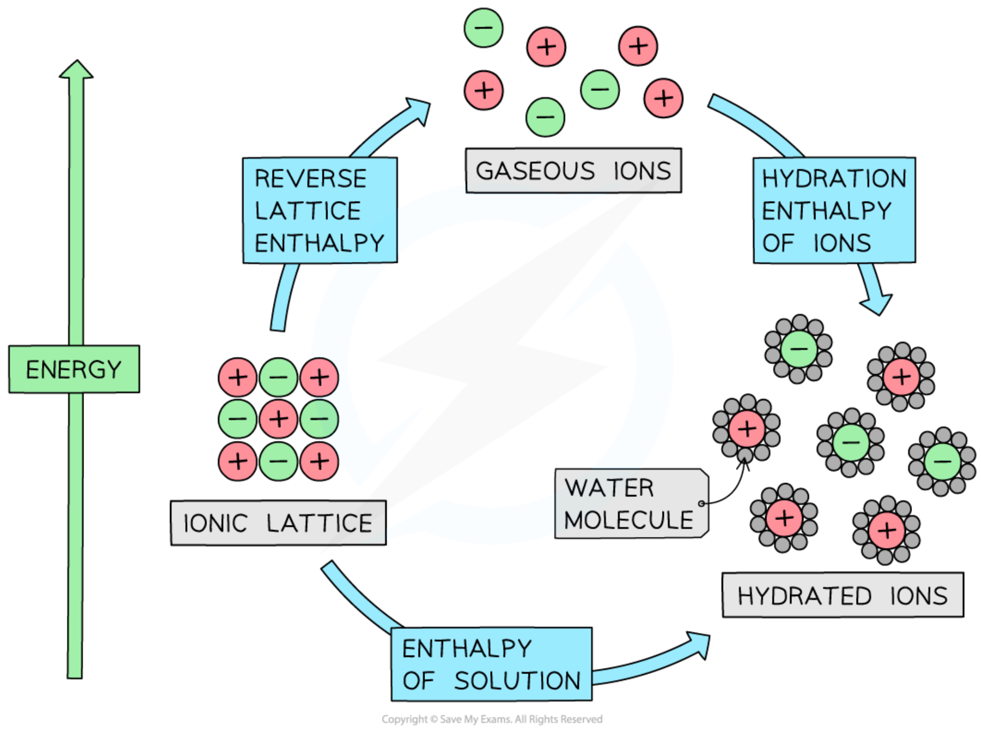
The polar water molecules will form ion-dipole bonds with the ions in solution (a) causing the ions to become hydrated (b)

Your notes

Energy Cycle Using Enthalpy Changes & Lattice Energy

- The standard enthalpy change of hydration (ΔH_{hyd}^{θ}) can be calculated by constructing **energy cycles** and applying Hess's law

Example energy cycle



Energy cycle involving enthalpy change of solution, lattice energy, and enthalpy change of hydration

- The energy cycle shows that there are two routes to go from the ionic lattice to the hydrated ions in an aqueous solution:
  - **Route 1**: going from ionic solid → ions in aqueous solution (this is the **direct route**)

ΔH_{sol}^{θ} = enthalpy of solution

- **Route 2**: going from ionic lattice → gaseous ions → ions in aqueous solution (this is the **indirect route**)

$-\Delta H_{latt}^{\theta} + \Delta H_{hyd}^{\theta}$ = reverse lattice enthalpy + hydration enthalpies of each ion

- Lattice enthalpy usually means Lattice *formation* enthalpy, in other words bond forming
  - If we are breaking the lattice then this is reversing the enthalpy change so a negative sign is added in front of the term (alternatively it is called lattice *dissociation*

enthalpy)

- According to **Hess's law,** the enthalpy change for both routes is the same, such that:

$$\Delta H_{sol}^{\theta} = -\Delta H_{latt}^{\theta} + \Delta H_{hyd}^{\theta}$$

$$\Delta H_{hyd}^{\theta} = \Delta H_{sol}^{\theta} + \Delta H_{latt}^{\theta}$$

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

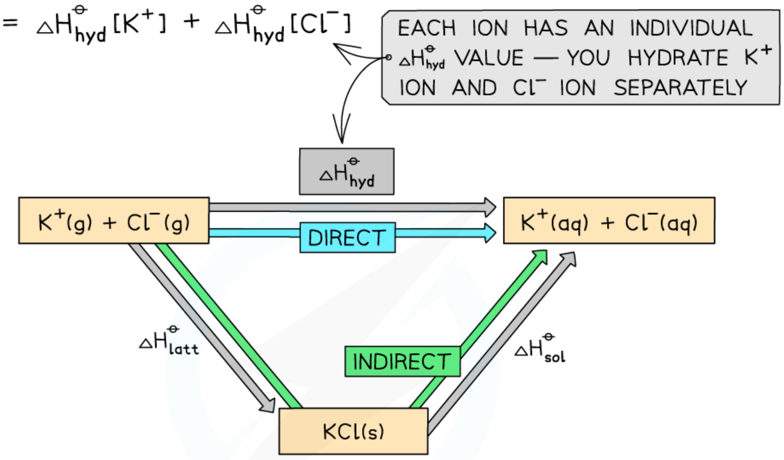
Worked Example

Construct an energy cycle and energy level diagram to calculate the ΔH_{hyd}^{θ} of the chloride ion in KCl.

Answer:

- Energy cycle:

$$\therefore \Delta H_{hyd}^{\ominus} = \Delta H_{hyd}^{\ominus}[K^+] + \Delta H_{hyd}^{\ominus}[Cl^-]$$



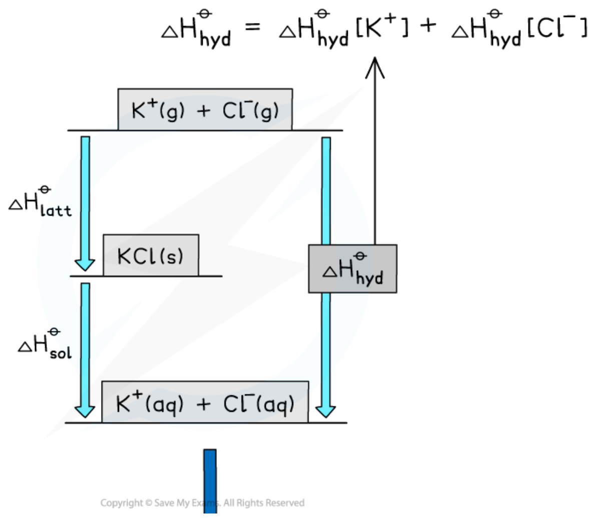
$$\Delta H_{hyd}^{\ominus} = \Delta H_{latt}^{\ominus}[KCl] + \Delta H_{sol}^{\ominus}[KCl]$$

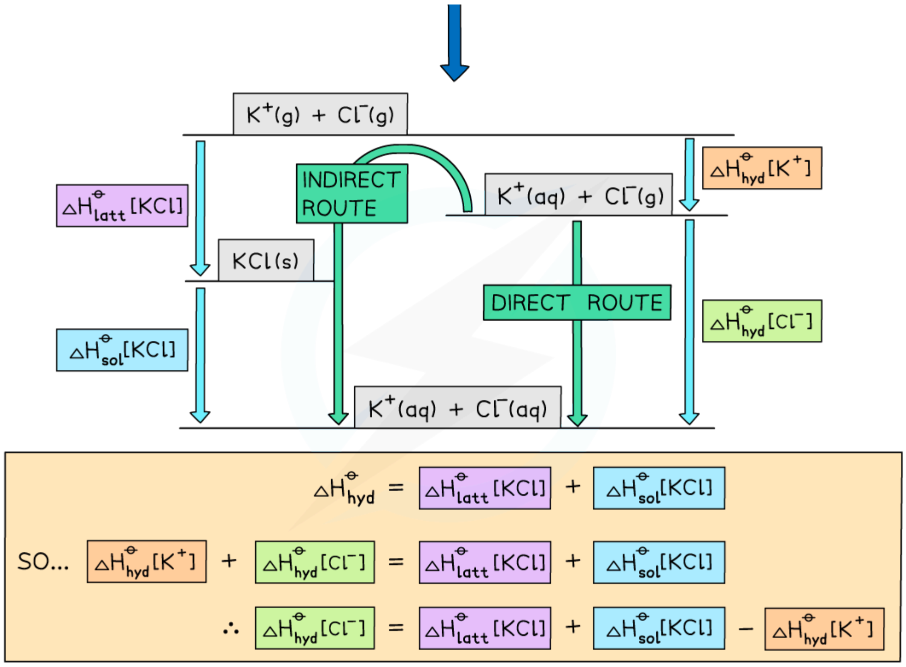
$$\Delta H_{hyd}^{\ominus}[K^+] + \Delta H_{hyd}^{\ominus}[Cl^-] = \Delta H_{latt}^{\ominus}[KCl] + \Delta H_{sol}^{\ominus}[KCl]$$

$$\therefore \Delta H_{hyd}^{\ominus}[Cl^-] = \Delta H_{latt}^{\ominus}[KCl] + \Delta H_{sol}^{\ominus}[KCl] - \Delta H_{hyd}^{\ominus}[K^+]$$

- Energy level diagram:

Your notes





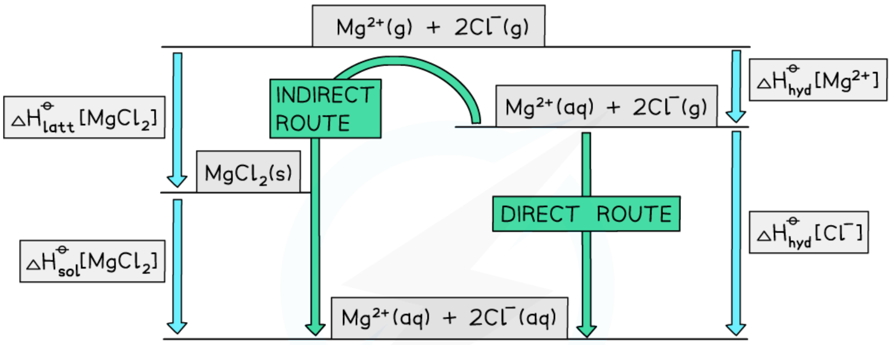
Your notes

Worked Example

Construct an energy cycle and energy level diagram to calculate the $\Delta H hyd^{\theta}$ of magnesium ions in magnesium chloride.

Answer:

- Energy cycle:

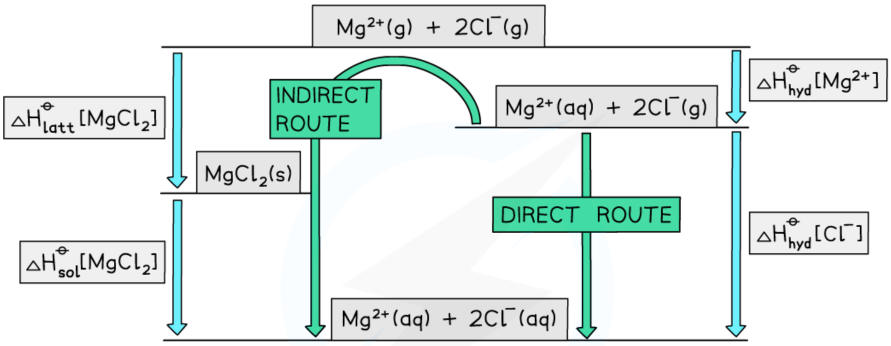


$$\Delta H^{\ominus}_{hyd} = \Delta H^{\ominus}_{latt}[MgCl_2] + \Delta H^{\ominus}_{sol}[MgCl_2]$$

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

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

- Energy level diagram:



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

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

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

Your notes

Energy Cycle Calculations

- The energy cycle involving the enthalpy change of solution (ΔH_{sol}^{θ}), lattice energy (ΔH_{latt}^{θ}), and enthalpy change of hydration (ΔH_{hyd}^{θ}) can be used to calculate the different enthalpy values
- According to Hess's law, the enthalpy change of the direct and of the indirect route will be the same, such that:

$$\Delta H_{hyd}^{\theta} = \Delta H_{latt}^{\theta} + \Delta H_{sol}^{\theta}$$

- This equation can be rearranged depending on which enthalpy value needs to be calculated
- For example, ΔH_{latt}^{θ} can be calculated using:

$$\Delta H_{latt}^{\theta} = \Delta H_{hyd}^{\theta} - \Delta H_{sol}^{\theta}$$

- **Remember**: the total ΔH_{hyd}^{θ} is found by adding the ΔH_{hyd}^{θ} values of both anions and cations together
- **Remember:** take into account the number of each ion when completing calculations
  - For example, $MgCl_2$ has **two chloride ions**, so when completing calculations this will need to be accounted for
  - In this case, you would need to double the value of the hydration enthalpy, since you are hydrating **2 moles** of chloride ions instead of 1

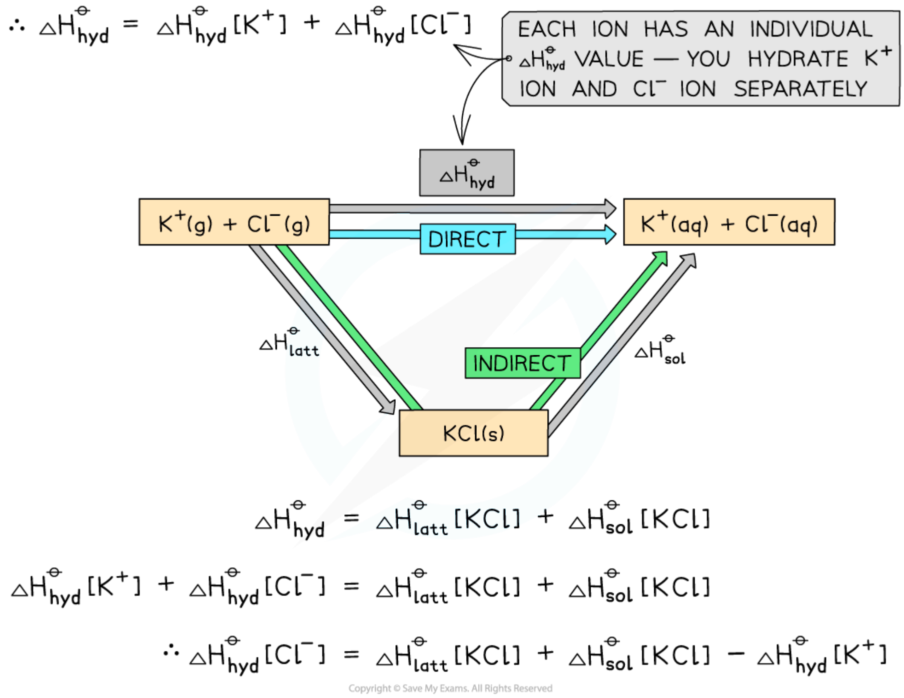
Worked Example

Calculate the ΔH^{θ} of the chloride ion in potassium chloride using the following data:

- ΔH_{latt}^{θ} [KCl] = -711 kJ mol^{-1}
- ΔH_{sol}^{θ} [KCl] = +26 kJ mol^{-1}
- ΔH_{hyd}^{θ} [K^+] = -322 kJ mol^{-1}

Answer:

- **Step 1:** Draw the energy cycle of KCl



- **Step 2:** Apply Hess's law to find $\Delta H_{hyd}{}^{\theta}$ $[Cl^-]$
  - $\Delta H_{hyd}{}^{\theta} = (\Delta H_{latt}{}^{\theta}[KCl]) + (\Delta H_{sol}{}^{\theta}[KCl])$
  - $(\Delta H_{hyd}{}^{\theta}[K^+]) + (\Delta H_{hyd}{}^{\theta}[Cl^-]) = (\Delta H_{latt}{}^{\theta}[KCl]) + (\Delta H_{sol}{}^{\theta}[KCl])$
  - $(\Delta H_{hyd}{}^{\theta}[Cl^-]) = (\Delta H_{latt}{}^{\theta}[KCl]) + (\Delta H_{sol}{}^{\theta}[KCl]) - (\Delta H_{hyd}{}^{\theta}[K^+])$
- **Step 3:** Substitute the values to find $\Delta H_{hyd}{}^{\equiv}$ $[Cl^-]$
  - $\Delta H_{hyd}{}^{\theta}$ $[Cl^-]$ = (-711) + (+26) - (-322) = -363 kJ mol^{-1}

Worked Example

Calculate the $\Delta H^{\theta}{}_{hyd}$ of the magnesium ion in the magnesium chloride using the following data:

- $\Delta H_{latt}{}^{\theta}$ $[MgCl_2]$ = -2592 kJ mol^{-1}
- $\Delta H_{sol}{}^{\theta}$ $[MgCl_2]$ = -55 kJ mol^{-1}
- $\Delta H_{hyd}{}^{\theta}$ $[Cl^-]$ = -363 kJ mol^{-1}

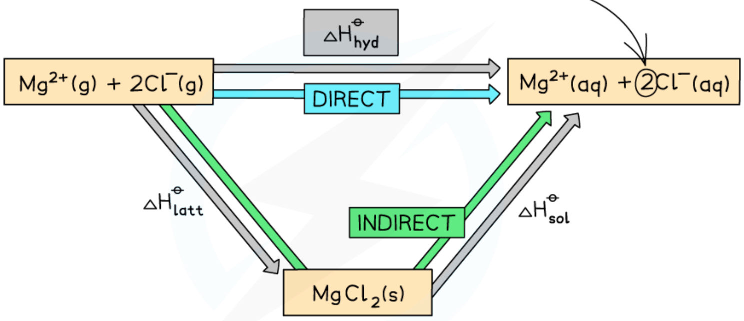
Answer:

- **Step 1:** Draw the energy cycle of $MgCl_2$

Your notes

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

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:** Apply Hess's law to find $\Delta H_{hyd}^{\equiv}$ $[Mg^{2+}]$
  - $\Delta H_{hyd}^{\theta} = (\Delta H_{latt}^{\theta}[MgCl_2]) + (\Delta H_{sol}^{\theta}[MgCl_2])$
  - $(\Delta H_{hyd}^{\theta}[Mg^{2+}]) + (2\Delta H_{hyd}^{\theta}[Cl^{-}]) = (\Delta H_{latt}^{\theta}[MgCl_2]) + (\Delta H_{sol}^{\theta}[MgCl_2])$
  - $(\Delta H_{hyd}^{\theta}[Mg^{2+}]) = (\Delta H_{latt}^{\theta}[MgCl_2]) + (\Delta H_{sol}^{\theta}[MgCl_2]) - (2\Delta H_{hyd}^{\theta}[Cl^{-}])$
- **Step 3:** Substitute the values to find $\Delta H_{hyd}^{\theta}[Mg^{2+}]$
  - $\Delta H_{hyd}^{\theta}[Mg^{2+}] = (-2592) + (-55) - (2 \times -363) = -1921$ kJ mol^{-1}

Your notes

Your notes

Enthalpy of Hydration: Ionic Charge & Radius

- The standard enthalpy change of hydration (ΔH_{hyd}^{θ}) is affected by the amount that the ions are attracted to the water molecules
- The factors which affect this attraction are the **ionic charge** and **radius**

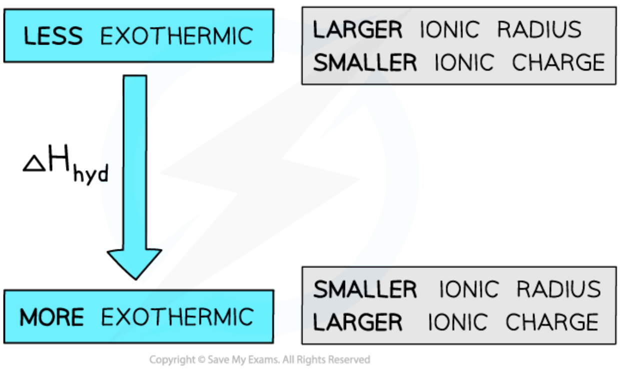
Ionic radius

- The standard enthalpy change of hydration (ΔH_{hyd}^{θ}) becomes **more exothermic** (more negative) as the **ionic radius decreases**
- Smaller ions have a **higher charge density**, resulting in stronger **ion–dipole attractions** with water molecules
- Therefore, **more energy is released** when these ions are hydrated
- **For example:**
    - Mg^{2+} in $MgSO_4$ is smaller than Ba^{2+} in $BaSO_4$
    - As a result, ΔH_{hyd}^{θ} **of $MgSO_4$ is more exothermic** than that of $BaSO_4$

Ionic charge

- The enthalpy of hydration becomes **more exothermic** as the **ionic charge increases**
- Higher charge leads to a **greater charge density**, strengthening ion–dipole attractions with water molecules
- This means **more energy is released** during hydration
- **For example:**
    - Ca^{2+} and O^{2-} in CaO have higher charges than K^+ and Cl^- in KCl
    - Therefore, **ΔH_{hyd}^{θ} of CaO is more exothermic** than that of KCl

Comparing enthalpies of hydration



The enthalpy of hydration is more exothermic for smaller ions and ions with a greater ionic charge

Your notes