



Enthalpies of Solution & Hydration

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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:



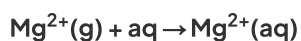
OR



- 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, $+711 \text{ kJ mol}^{-1}$ is needed
- However, the ΔH_{sol}^θ of KCl is $+26 \text{ kJ mol}^{-1}$
- This means that another $+685 \text{ kJ mol}^{-1}$ ($711 - 26$) 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



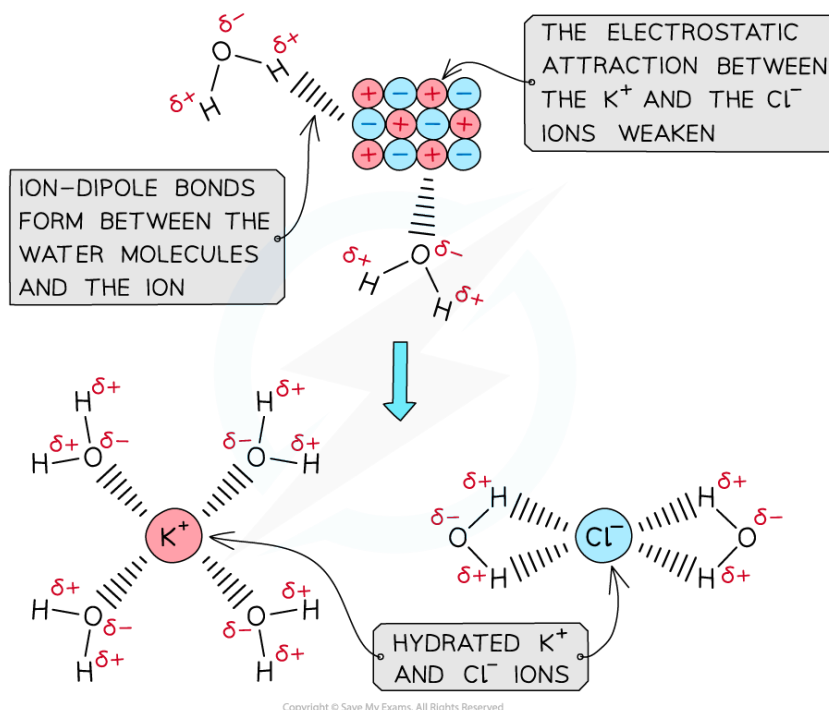
- Hydration enthalpies are the measure of the energy that is released when there is an attraction formed between the ions and water molecules
 - Hydration enthalpies are **exothermic**

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)



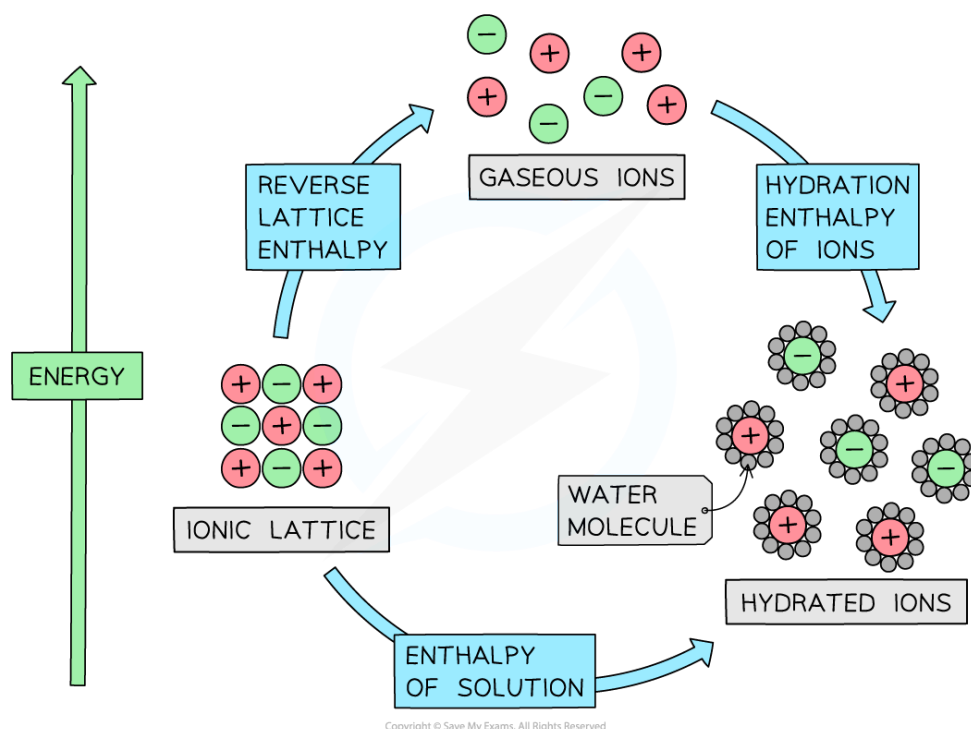
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Energy Cycle Using Enthalpy Changes & Lattice Energy

- 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 \rightarrow ions in aqueous solution (this is the **direct route**)

$$\Delta H_{sol}^\theta = \text{enthalpy of solution}$$
 - Route 2:** going from ionic lattice \rightarrow gaseous ions \rightarrow ions in aqueous solution (this is the **indirect route**)

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

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

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

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



Your notes



Worked Example

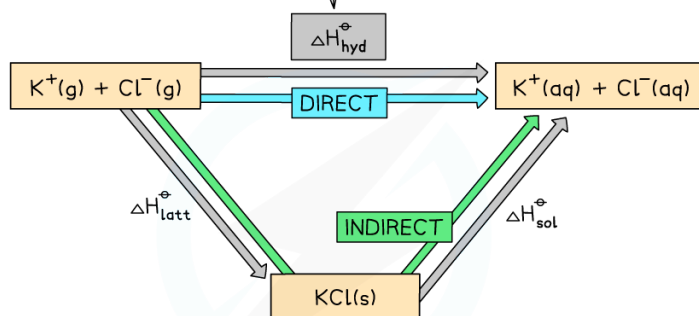
Construct an energy cycle and energy level diagram to calculate the $\Delta H_{\text{hyd}}^{\ominus}$ of the chloride ion in KCl.

Answer:

- Energy cycle:

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

EACH ION HAS AN INDIVIDUAL $\Delta H_{\text{hyd}}^{\ominus}$ VALUE — YOU HYDRATE K^+ ION AND Cl^- ION SEPARATELY



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

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

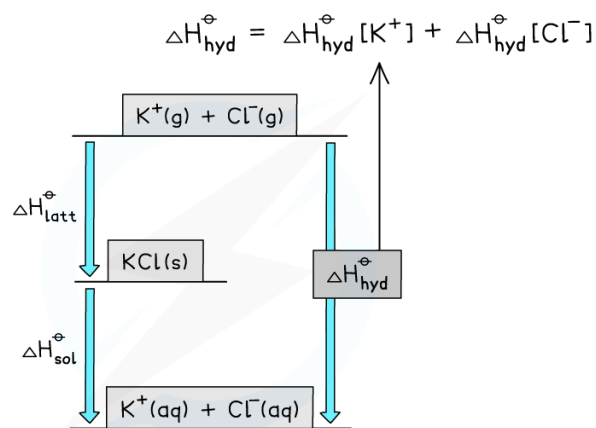
$$\therefore \Delta H_{\text{hyd}}^{\ominus} [\text{Cl}^-] = \Delta H_{\text{latt}}^{\ominus} [\text{KCl}] + \Delta H_{\text{sol}}^{\ominus} [\text{KCl}] - \Delta H_{\text{hyd}}^{\ominus} [\text{K}^+]$$

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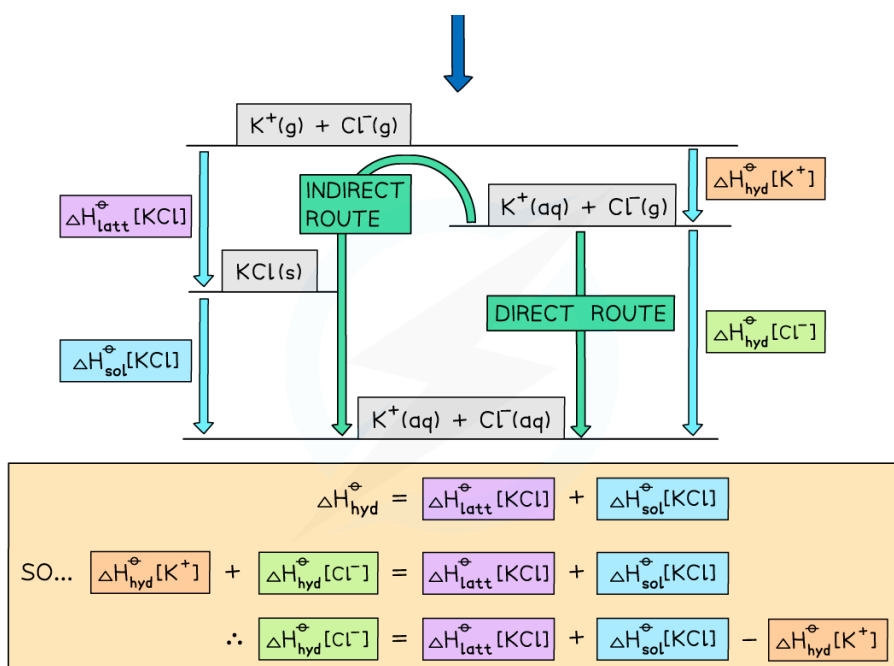
- Energy level diagram:



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Worked Example

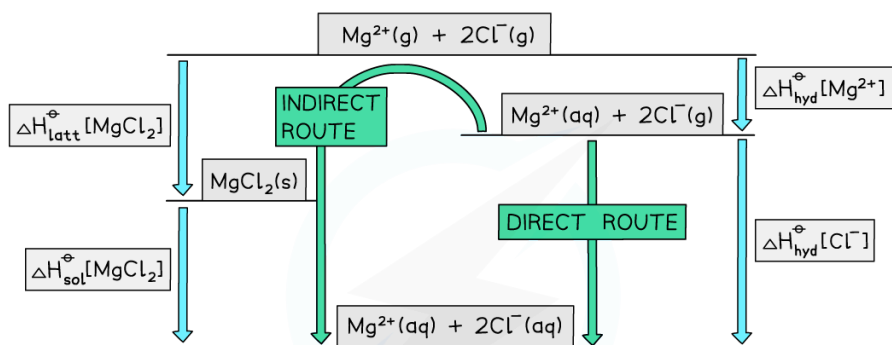
Construct an energy cycle and energy level diagram to calculate the $\Delta H_{\text{hyd}}^{\ominus}$ of magnesium ions in magnesium chloride.

Answer:

- Energy cycle:



Your notes



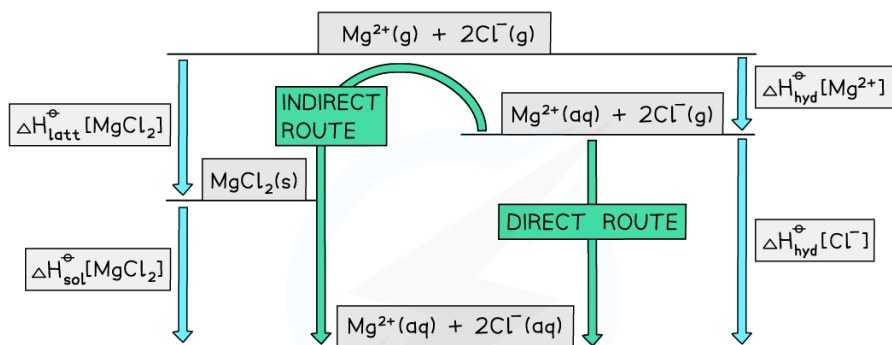
$$\Delta H_{\text{hyd}}^{\ominus} = \Delta H_{\text{latt}}^{\ominus}[\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus}[\text{MgCl}_2]$$

$$\Delta H_{\text{hyd}}^{\ominus}[\text{Mg}^{2+}] + 2\Delta H_{\text{hyd}}^{\ominus}[\text{Cl}^{-}] = \Delta H_{\text{latt}}^{\ominus}[\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus}[\text{MgCl}_2]$$

$$\Delta H_{\text{hyd}}^{\ominus}[\text{Mg}^{2+}] = \Delta H_{\text{latt}}^{\ominus}[\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus}[\text{MgCl}_2] - 2\Delta H_{\text{hyd}}^{\ominus}[\text{Cl}^{-}]$$

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- Energy level diagram:



$$\Delta H_{\text{hyd}}^{\ominus} = \Delta H_{\text{latt}}^{\ominus}[\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus}[\text{MgCl}_2]$$

$$\Delta H_{\text{hyd}}^{\ominus}[\text{Mg}^{2+}] + 2\Delta H_{\text{hyd}}^{\ominus}[\text{Cl}^{-}] = \Delta H_{\text{latt}}^{\ominus}[\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus}[\text{MgCl}_2]$$

$$\Delta H_{\text{hyd}}^{\ominus}[\text{Mg}^{2+}] = \Delta H_{\text{latt}}^{\ominus}[\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus}[\text{MgCl}_2] - 2\Delta H_{\text{hyd}}^{\ominus}[\text{Cl}^{-}]$$

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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:

- $\Delta H_{latt}^\theta [\text{KCl}] = -711 \text{ kJ mol}^{-1}$
- $\Delta H_{sol}^\theta [\text{KCl}] = +26 \text{ kJ mol}^{-1}$
- $\Delta H_{hyd}^\theta [\text{K}^+] = -322 \text{ kJ mol}^{-1}$

Answer:

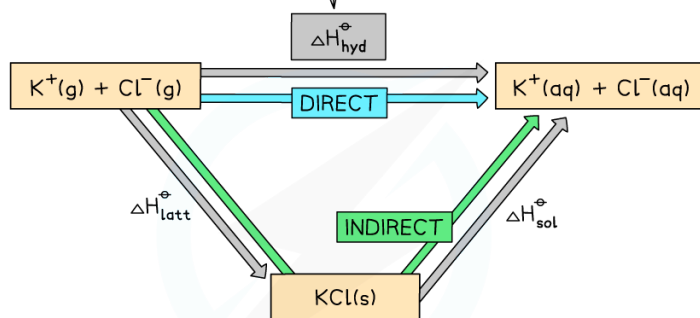
- Step 1:** Draw the energy cycle of KCl



Your notes

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

EACH ION HAS AN INDIVIDUAL $\Delta H_{\text{hyd}}^{\ominus}$ VALUE — YOU HYDRATE K^+ ION AND Cl^- ION SEPARATELY



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

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

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

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



Worked Example

Calculate the $\Delta H_{\text{hyd}}^{\ominus}$ of the magnesium ion in the magnesium chloride using the following data:

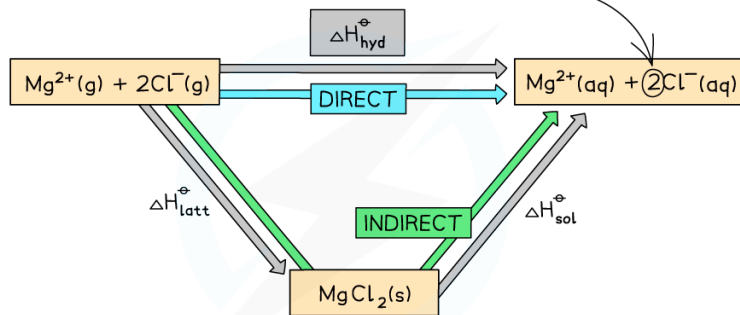
- $\Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_2] = -2592 \text{ kJ mol}^{-1}$
- $\Delta H_{\text{sol}}^{\ominus} [\text{MgCl}_2] = -55 \text{ kJ mol}^{-1}$
- $\Delta H_{\text{hyd}}^{\ominus} [\text{Cl}^-] = -363 \text{ kJ mol}^{-1}$

Answer:

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

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

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



$$\Delta H_{\text{hyd}}^{\ominus} = \Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus} [\text{MgCl}_2]$$

$$\Delta H_{\text{hyd}}^{\ominus} [\text{Mg}^{2+}] + 2\Delta H_{\text{hyd}}^{\ominus} [\text{Cl}^{-}] = \Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus} [\text{MgCl}_2]$$

$$\therefore \Delta H_{\text{hyd}}^{\ominus} [\text{Mg}^{2+}] = \Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_2] + \Delta H_{\text{sol}}^{\ominus} [\text{MgCl}_2] - 2\Delta H_{\text{hyd}}^{\ominus} [\text{Cl}^{-}]$$

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- **Step 2:** Apply Hess's law to find $\Delta H_{\text{hyd}}^{\ominus} [\text{Mg}^{2+}]$

- $\Delta H_{\text{hyd}}^{\ominus} = (\Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_2]) + (\Delta H_{\text{sol}}^{\ominus} [\text{MgCl}_2])$
- $(\Delta H_{\text{hyd}}^{\ominus} [\text{Mg}^{2+}]) + (2\Delta H_{\text{hyd}}^{\ominus} [\text{Cl}^{-}]) = (\Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_2]) + (\Delta H_{\text{sol}}^{\ominus} [\text{MgCl}_2])$
- $(\Delta H_{\text{hyd}}^{\ominus} [\text{Mg}^{2+}]) = (\Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_2]) + (\Delta H_{\text{sol}}^{\ominus} [\text{MgCl}_2]) - (2\Delta H_{\text{hyd}}^{\ominus} [\text{Cl}^{-}])$

- **Step 3:** Substitute the values to find $\Delta H_{\text{hyd}}^{\ominus} [\text{Mg}^{2+}]$

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



Your notes



Enthalpy of Hydration: Ionic Charge & Radius

- The standard enthalpy change of hydration (ΔH_{hyd}^{\ominus}) 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**

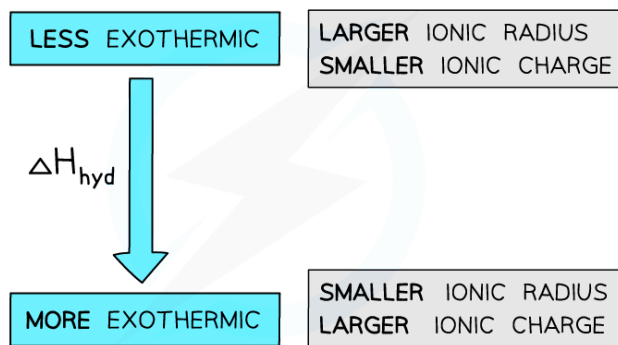
Ionic radius

- The standard enthalpy change of hydration (ΔH_{hyd}^{\ominus}) 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}^{\ominus} 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}^{\ominus} of CaO is **more exothermic** than that of KCl

Comparing enthalpies of hydration



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



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