

Exercise walk-through

23.2

Enthalpies of solution and hydration

A-Level Chemistry

Entropy ΔS

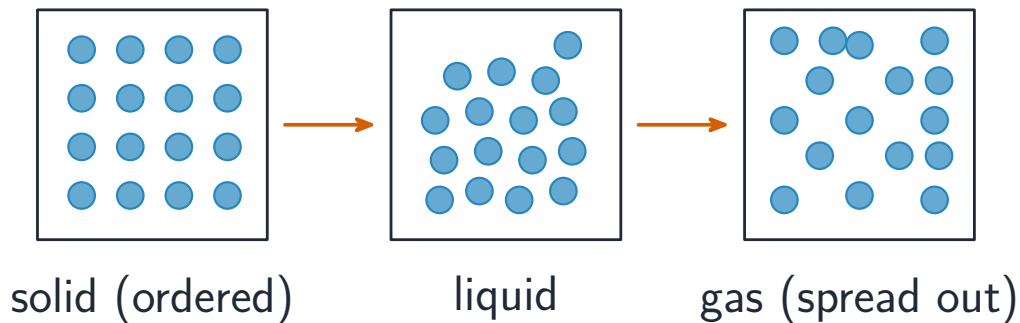
Entropy measures the number of arrangements (“disorder”).

■ solid $\rightarrow$ liquid $\rightarrow$ gas, dissolving: $\Delta S > 0$

■ more gas molecules: $\Delta S > 0$

$$\Delta S^{\ominus} = \sum S^{\ominus}_{\text{products}} - \sum S^{\ominus}_{\text{reactants}}$$

entropy increases: $\Delta S > 0$



Calculating entropy change, and feasibility

from standard entropies

$$\Delta S^{\ominus} = \sum S^{\ominus}(\text{products}) - \sum S^{\ominus}(\text{reactants})$$

the units

$\text{J K}^{-1}\text{mol}^{-1}$ – joules, while ΔH is in kilojoules

the sign

predict it first from the change in moles of gas

Gibbs free energy

$$\Delta G = \Delta H - T\Delta S, \text{ with } T \text{ in kelvin}$$

feasible

when $\Delta G \leq 0$

the feasibility temperature

set $\Delta G = 0$: $T = \frac{\Delta H}{\Delta S}$ – the temperature at which it becomes possible

Convert ΔS from joules to kilojoules before substituting. That factor of 1000 is the single commonest error in this whole topic.

Gibbs free energy ΔG

	ΔS positive	ΔS negative
ΔH neg.	feasible at all temperatures	feasible only at low temperature
ΔH pos.	feasible only at high temperature	never feasible

$\Delta G = \Delta H - T\Delta S$; **feasible when $\Delta G \leq 0$**

Gibbs free
energy :

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

A reaction is **feasible** when $\Delta G \leq 0$. Whether it is can depend on temperature.

ΔG : worked example

$$\Delta H = +120 \text{ kJ mol}^{-1}, \Delta S = +0.200 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{at } 298 \text{ K: } \Delta G = 120 - 298 \times 0.200 = +60 \text{ kJ mol}^{-1} \text{ (not yet feasible)}$$

$$\text{Set } \Delta G = 0: T = \frac{\Delta H}{\Delta S} = \frac{120}{0.200} = 600 \text{ K} - \text{feasible above } 600 \text{ K.}$$

Enthalpies of solution and hydration, continued



An instant cold pack feels cold because its salt dissolves endothermically (a positive ΔH_{sol}), driven by the rise in entropy

Exercises 2.1-2.2

2.1 Define **enthalpy change of hydration**.

[2]

2.2 State **two** factors that make hydration of an ion more exothermic.

[2]

Exercises 2.1·2.2

2.1 Define **enthalpy change of hydration**.

[2]

2.1

- the enthalpy change when 1 mol of gaseous ions is dissolved in (a large amount of) water

2.2 State **two** factors that make hydration of an ion more exothermic.

[2]

2.2

- a higher ionic charge; a smaller ionic radius

Exercises 3.1-3.2

3.1 Enthalpy of hydration is most exothermic for:

[1]

☐

A a large, singly-charged ion

B a small, highly-charged ion

C a large, highly-charged ion

D a neutral atom

3.2 Which equation correctly links the enthalpies?

[1]

☐

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

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

C $\Delta H_{\text{sol}} = \Delta H_{\text{latt}} - \Delta H_{\text{hyd}}$

D $\Delta H_{\text{sol}} = -\Delta H_{\text{hyd}}$

Exercises 3.1·3.2

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- A a large, singly-charged ion
- B a small, highly-charged ion
- C a large, highly-charged ion
- D a neutral atom

3.1 B

- A small, highly-charged ion has the highest charge density, so the most exothermic hydration

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3.2 B

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

Exercise 3.3 (a)

3.3 For a salt, $\Delta H_{\text{latt}} = -780 \text{ kJ mol}^{-1}$ and the sum of the hydration enthalpies of its ions is -820 kJ mol^{-1} .

(a) Calculate the enthalpy change of solution.

[2]

Exercise 3.3 (a)

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[2]

(a)

- $\Delta H_{\text{sol}} = -(-780) + (-820) = +780 - 820 = -40 \text{ kJ mol}^{-1}$

Exercise 3.3 (b)

3.3 For a salt, $\Delta H_{\text{latt}} = -780 \text{ kJ mol}^{-1}$ and the sum of the hydration enthalpies of its ions is -820 kJ mol^{-1} .

(b) State whether the salt dissolving is exothermic or endothermic. [1]

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(b)

- exothermic

Exercise 3.4

3.4 Explain why the hydration enthalpy of Mg^{2+} is more exothermic than that of Na^+ . [2]

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3.4

- Mg^{2+} has a higher charge and a smaller radius than Na^+ , so a higher charge density that attracts the polar water molecules more strongly – more exothermic hydration

Exercise 3.5 (a)

3.5 The table gives data for two Group 2 chlorides.

	$\Delta H_{\text{LE}}^{\ominus} / \text{kJ mol}^{-1}$	$\Delta H_{\text{sol}}^{\ominus} / \text{kJ mol}^{-1}$
MgCl ₂	−2526	−155
CaCl ₂	−2258	−83

$$\Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^{-}) = -364 \text{ kJ mol}^{-1}.$$

(a) Draw the energy cycle linking lattice enthalpy, enthalpy of solution and the enthalpies of hydration, and use it to calculate $\Delta H_{\text{hyd}}^{\ominus}(\text{Mg}^{2+})$. [5]

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- The cycle goes: solid $\rightarrow$ gaseous ions ($-\Delta H_{\text{LE}}$) $\rightarrow$ aqueous ions ($\sum \Delta H_{\text{hyd}}$), and directly solid $\rightarrow$ aqueous ions (ΔH_{sol}). So $\Delta H_{\text{sol}} = -\Delta H_{\text{LE}} + \Delta H_{\text{hyd}}(\text{Mg}^{2+}) + 2\Delta H_{\text{hyd}}(\text{Cl}^{-})$; $-155 = 2526 + \Delta H_{\text{hyd}}(\text{Mg}^{2+}) + 2(-364)$; $\Delta H_{\text{hyd}}(\text{Mg}^{2+}) = -155 - 2526 + 728 = -1953 \text{ kJ mol}^{-1}$

Exercise 3.5 (b)

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(b)

- Mg²⁺ is the smaller ion but carries the same 2+ charge, so it has the greater charge density; it attracts the δ^{-} oxygen of the water molecules more strongly, releasing more energy per mole

Exercise 3.5 (c)

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(c) Both dissolvings are exothermic, yet the magnitudes are small compared with the individual terms. Explain why. [2]

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- ΔH_{sol} is the small **difference** between two very large opposing terms – the energy needed to pull the lattice apart and the energy released on hydration; they nearly cancel, so the net value is small

Exercise 3.5 (d)

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(d)

- The purely ionic model assumes perfect spheres with no covalent character; a small, highly charged cation polarises a large anion, giving some covalent character and a larger experimental lattice enthalpy than calculated