

CHEMISTRY

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [] at the end of each question, or part question.

This document consists a total of **10** printed pages.

- 1 (a) Unionised sulfuric acid is a volatile liquid at standard conditions. With appropriate chemical equations whose enthalpy change reflect the terms below, define the following for unionised sulfuric acid:

- (i) *standard enthalpy change of atomisation;* [2]



B1 – Energy required to form the constituent atoms of unionised sulfuric acid from itself, per mole of unionised sulfuric acid, at 298 K, 1 bar.

- (ii) *standard enthalpy change of formation;* [2]

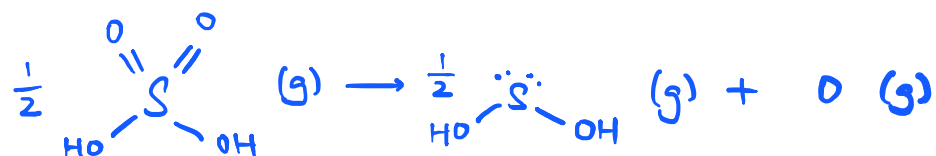


B1 – Enthalpy change when 1 mole of unionised sulfuric acid is formed from its constituent elements - 1 mole of sulfur, 2 moles of oxygen and 1 mole of hydrogen - at 298 K, 1 bar.

(Accept S_8 as an alternative)

- (iii) *and the bond energy of the S=O bond.* [2]

B1 – Correct chemical equation which indicates S=O bond being broken only (drawing structural formula is hence clearer)



B1 – Half the energy required to break both S=O bonds homolytically per mole of gaseous H_2SO_4 .

(Accept “average” although since there are 2 bonds, half is more ideal)

All state symbols must be present for each equation.
The stoichiometric coefficient for H₂SO₄ must be 1 for (i) and (ii), and ½ for (iii)!
No partial credit awarded for definitions and chemical equation.
Answers must be contextualised to H₂SO₄! Generic descriptions score zero.

- (b) When water is added to unionised sulfuric acid, the resultant solution increases in temperature, releasing enough heat to cause vigorous boiling.
- (i) With reference to bond formation, interactions and reactions between sulfuric acid and water molecules, explain the above observation. [2]

B1 - Sulfuric acid ionises fully in water to form SO₄²⁻ and H⁺ ions.
B1 - **Strong** ion-dipole interactions between water and the ions results in large amounts of heat/energy being released. (word 'strong' is needed to explain why so much heat was released)

Reject hydrogen bonds because sulfuric acid is a strong acid.

- (ii) Suggest whether you should make a solution of aqueous sulfuric acid of a dilute concentration by
- adding unionised sulfuric acid to water;
 - **or** adding water to unionised sulfuric acid. [1]

B1 - Adding unionised sulfuric acid to water

No reason is required

(To make a dilute solution, you need to add the acid to water because if you add water to acid, the first bits of water will start to boil off causing vigorous splashing)

- (c) Unionised sulfuric acid is a dehydrating agent. For example, under strong heating at 425 to 450 K, ethanol is converted to ethene. You should assume that at these conditions, both molecules are gases.
- (i) Calculate the enthalpy change of this dehydration reaction in such conditions. [2]

Ethanol: C₂H₅OH; Ethene: C₂H₄

Enthalpy change of vapourisation of liquid water: +41.0 kJ mol⁻¹

M1 – Shows working for correct bonds formed and broken

Bonds broken – 1 C—O, 1 C—C, 1 C—H

Bonds formed – 1 C=C, 1 O—H

A1 – Correct answer

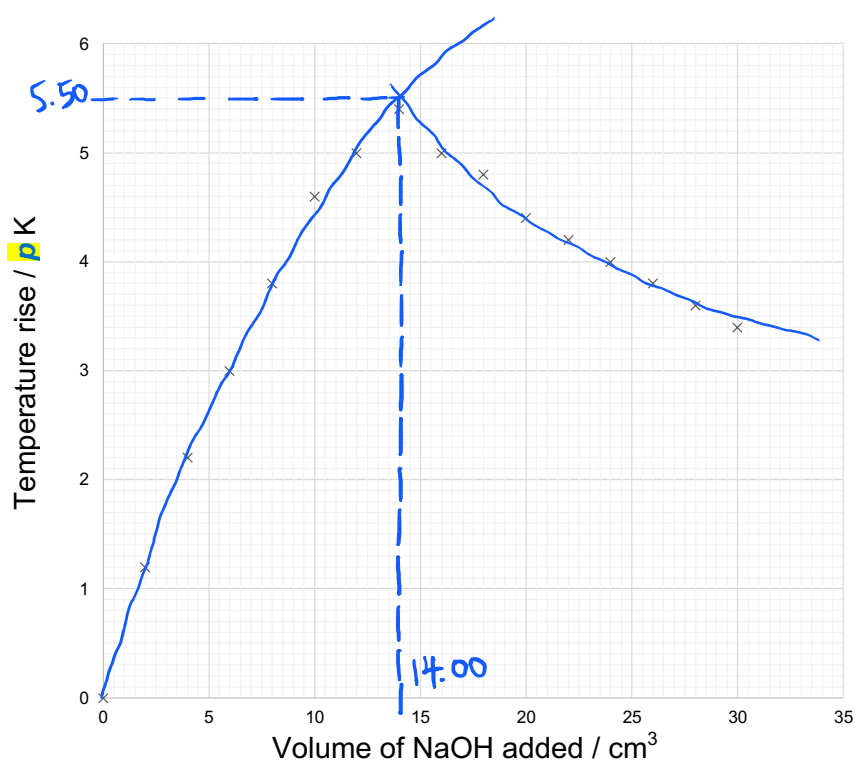
Note that water is a gas at 425 to 450 K!

$$\Delta H = 360 + 350 + 410 - 610 - 460 = +50 \text{ kJ mol}^{-1}$$

- (ii) Explain whether the entropy change of this reaction is positive or negative. [1]

B1 – Positive because of the increase in the number of moles of gas formed (from 1 to 2 per mole of equation), resulting in more ways to distribute energy within the system.

- (d) 25.0 cm³ of 1.00 mol dm⁻³ aqueous sulfuric acid was titrated against a solution of sodium hydroxide. The temperature rise of the solution against volume of NaOH added was recorded, and plotted on the graph below. You should assume that there was no heat loss or gain from the surroundings.



The enthalpy change of neutralisation is -57.1 kJ mol⁻¹.

- (i) Determine the concentration of NaOH. [2]

M1 – Draws 2 best-fit curves and finds point of intersection

Best-fit curves should have an equal spread

MA1 – The below

$$n_{\text{H}^+} = \frac{25.0}{1000} \times 1.00 \times 2 = 0.0500 \text{ mol}$$

$$[\text{NaOH}] = \frac{0.0500}{\frac{14.00}{1000}} = 3.57 \text{ mol dm}^{-3}$$

- (ii) Determine p . Assume that the specific heat capacity of all solutions is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, and the density of all solutions is 1.00 g cm^{-3} . [2]

M1 – Calculates $q = 896.61p$

MA1 – Finds p

$$q = 0.0500 \times 57.1 \times 1000 = 2855 \text{ J}$$

and

$$q = mc\Delta T = (25.0 + 14.00) \times 1.00 \times 4.18 \times 5.50p = 896.61p \text{ J}$$

so

$$p = \frac{2855}{896.61} = 3.18$$

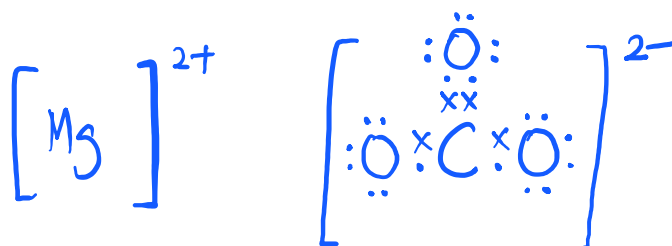
Note that p is a scaling factor for the vertical axis

- 2 This question is about Group 2 salts.

- (a) Draw the dot-and-cross diagram for magnesium carbonate. [1]

B1 – Correct dot-and-cross

There is no need to indicate the extra electrons for the carbonate anion.



- (b) The *lattice energy* of magnesium carbonate is $-3123 \text{ kJ mol}^{-1}$.

- (i) What is meant by the *lattice energy of magnesium carbonate*? [1]

B1 – Energy released when 1 mole of MgCO_3 is formed from its constituent gaseous ions, Mg^{2+} and CO_3^{2-} .

- (ii) Explain why the *lattice energy* of magnesium carbonate is negative. [1]

B1 – **Formation** of ionic bonds / electrostatic attraction releases energy.

- (c) The decomposition of magnesium carbonate was studied at 2 temperatures, to determine the ideal temperature for the industrial production of magnesium oxide. The products were bubbled into limewater and the observations are as follows:

Temperature / K	Effect on limewater
1050	White precipitate
400	No white precipitate

- (i) At a certain temperature, it was found that the reaction ceases to be feasible. Given the following data, determine this temperature. [2]

Compound	$\Delta S_f^\ominus / \text{J mol}^{-1} \text{K}^{-1}$
MgCO ₃ (s)	65.7
MgO(s)	26.9
CO ₂ (g)	213.6

The enthalpy change of the decomposition reaction is +100 kJ mol⁻¹.

M1 – Correct working

$$\Delta S = 26.9 + 213.6 - 65.7 = +174.8 \text{ J mol}^{-1} \text{K}^{-1}$$

MA1 – Correct answer with working

$$\Delta G = 0 = \Delta H - T\Delta S$$

$$T = \Delta H / \Delta S = 100000 / 174.8 = 572 \text{ K (3 s.f.)}$$

- (ii) Suggest the effect of increasing the temperature on the spontaneity of the reaction. [1]

B1 – Links ΔG to spontaneity based on the sign.

As long as the temperature is below 572 K, the reaction is not spontaneous because ΔG is positive.

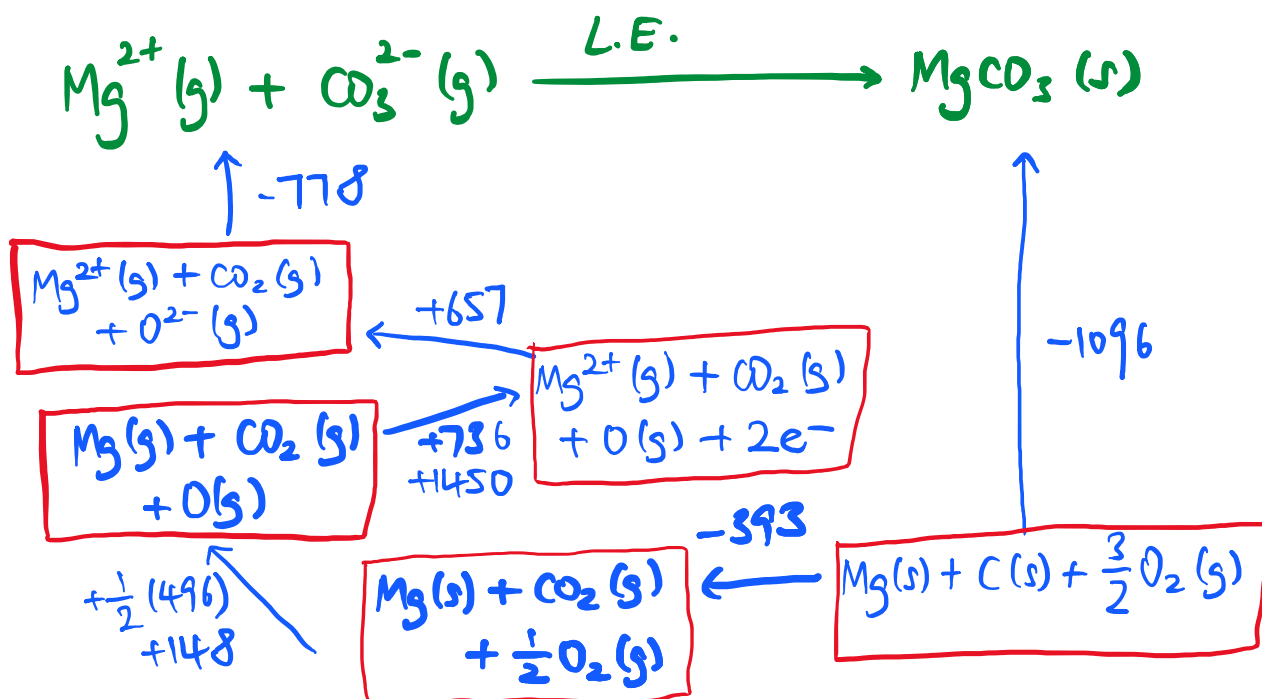
When the temperature increases beyond 572 K, the reaction remains spontaneous because ΔG is negative.

Reject 'more' or 'less' spontaneous. Spontaneity is a yes or no thing.

- (iii) Using the data provided and relevant data from the *Data Booklet*, construct an appropriate fully-labelled energy cycle to calculate the lattice energy of magnesium carbonate.

[4]

Enthalpy Term	$\Delta H / \text{kJ mol}^{-1}$
Enthalpy change of atomisation of magnesium	+148
Sum of 1 st and 2 nd electron affinities of oxygen	+657
Enthalpy change of formation of magnesium carbonate	-1096
Enthalpy change of formation of $\text{CO}_2(\text{g})$	-393
$\text{O}^{2-}(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{CO}_3^{2-}(\text{g})$	-778



M3 – Energy cycle shown

Penalise 0.5 pts up to 3 for each mistake

- No state symbols
- Copied wrong value(s) (0.5 pts per value)
- Missing one red boxes
- Swapping orders of red boxes (e.g. ionisation energy after electron affinity)

Allow arrows to point in other direction

Red boxes are for clarity, and should not be present in your working.

MA1 - L.E. = $-3160 \text{ kJ mol}^{-1}$ (working is needed, award ECF)

- (d) Data concerning some Group II sulfates and hydroxides, at 298 K, are given in the table below. Further data may be found in the *Data Booklet*.

	solubility / mol dm ⁻³	- lattice energy / kJ mol ⁻¹	$\Delta H_{\text{hydration}}$ of M ²⁺ / kJ mol ⁻¹	$\Delta H_{\text{hydration}}$ of SO ₄ ²⁻ / kJ mol ⁻¹
MgSO ₄	2.2	2959	-1890	-1160
CaSO ₄	1.5 x 10 ⁻²	2704	-1562	-1160
SrSO ₄	7.1 x 10 ⁻³	2572	-1414	-1160

	solubility / mol dm ⁻³	- lattice energy / kJ mol ⁻¹	$\Delta H_{\text{hydration}}$ of M ²⁺ / kJ mol ⁻¹	2 x $\Delta H_{\text{hydration}}$ of OH ⁻ / kJ mol ⁻¹
Mg(OH) ₂	1.6 x 10 ⁻⁴	2993	-1890	-1100
Ca(OH) ₂	2.5 x 10 ⁻²	2644	-1562	-1100
Sr(OH) ₂	3.4 x 10 ⁻²	2467	-1414	-1100

- (i) Define, with the aid of an equation, $\Delta H_{\text{hydration}}$ of M²⁺. Explain, with the aid of a labelled diagram, why $\Delta H_{\text{hydration}}$ of M²⁺ is negative. [4]

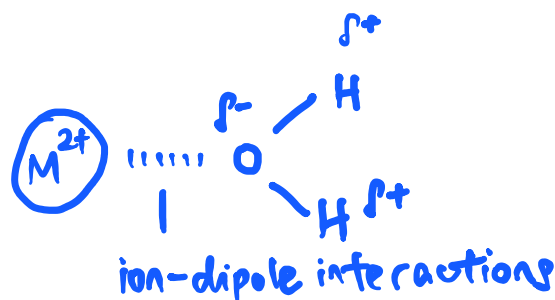
B1 – Correct equation: M²⁺ (g) → M²⁺ (aq)

B1 – Correct definition:

Energy released when 1 mole of gaseous M²⁺ is hydrated in an infinite amount of solvent (or water) forming 1 mole of aqueous M²⁺ (at 298 K, 1 bar).

Because there is no Plimsoll (⊖) sign that represents standard conditions, there is no need to indicate 298 K, 1 bar here.

A1 – Correct diagram illustrating ion-dipole interactions



A1 – **Formation** of ion-dipole interactions results in **energy** being **released** (exothermic reaction) and hence enthalpy change is negative.

- (ii) Explain why
- The magnitude of the lattice energy of Group II sulfates decreases from MgSO₄ to SrSO₄.
 - The $\Delta H_{\text{hydration}}$ of M²⁺ becomes less exothermic from Mg²⁺ to Sr²⁺. [2]

B1 each

- From Mg²⁺ to Sr²⁺ ionic radii increase. Considering same charge, L.E. becomes less negative since $\text{L.E.} \propto \frac{q_1 q_2}{r_1 + r_2}$.

OR

Less energy released because of weaker electrostatic attraction between opposite charged ions since the charge becomes more diffuse when ionic radii increase.

Reject any reference to charge density.

2. **Charge density decreases** because ionic radii increases → results in **poorer** ion-dipole interactions → less energy released.

(iii) Hence, suggest **qualitatively** why the solubility of Group II sulfates decreases from MgSO_4 to SrSO_4 , while the solubility of Group II hydroxides increases from Mg(OH)_2 to Sr(OH)_2 . [2]

B1 – Attempts to use $\Delta H_{\text{solution}} = -\text{L.E.} + \Delta H_{\text{hydration}}$

B1 – Attempts to explain via observation

For the sulfates, the -L.E. term becomes less positive, but the $\Delta H_{\text{hydration}}$ term becomes less negative **faster** down the group resulting in $\Delta H_{\text{solution}}$ becoming less negative.

For the hydroxides, the -L.E. term becomes less positive, but the $\Delta H_{\text{hydration}}$ term becomes less negative **slower** down the group resulting in $\Delta H_{\text{solution}}$ becoming more negative.

Why does the -L.E. term for hydroxides decrease more in magnitude compared to that of the sulfates?

It's probably because of the smaller ionic radius of the hydroxide ion.

Since $\text{L.E.} \propto \frac{q_1 q_2}{r_1 + r_2}$, for a smaller ionic radius, the $r_1 + r_2$ term increases (by proportion of itself) faster compared to when r_2 is for the sulfate ion.