Answer **all** the questions.

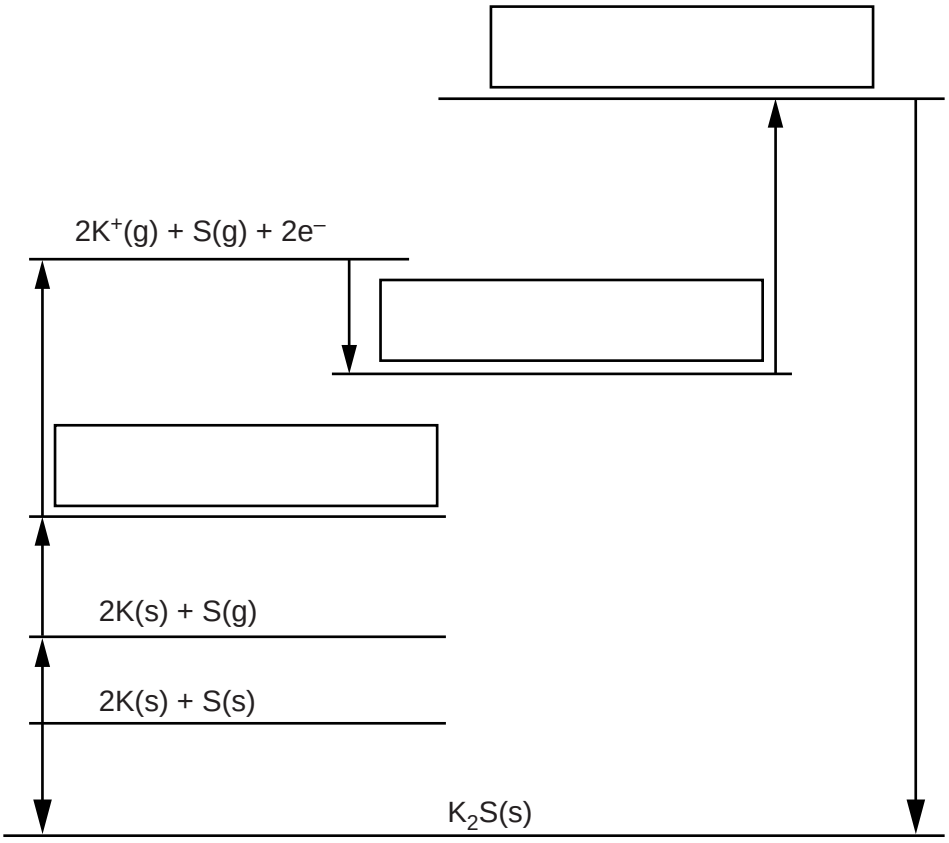
1 Born–Haber cycles can be used to calculate enthalpy changes indirectly.

(a) The table below shows enthalpy changes for a Born–Haber cycle involving potassium sulfide, K_2S.

	Enthalpy change / kJ mol^{-1}
Formation of potassium sulfide, K_2S	–381
1st electron affinity of sulfur	–200
2nd electron affinity of sulfur	+640
Atomisation of sulfur	+279
1st ionisation energy of potassium	+419
Atomisation of potassium	+89

(i) The incomplete Born–Haber cycle below can be used to determine the lattice enthalpy of potassium sulfide.

In the boxes, write the species present at each stage in the cycle.
Include state symbols for the species.



[3]

(ii) Define, in words, the term *lattice enthalpy*.

.....

.....

.....

..... **[2]**

(iii) Using the Born–Haber cycle, calculate the lattice enthalpy of potassium sulfide.

lattice enthalpy = ... $kJ\,mol^{-1}$ **[2]**

(b) Several ionic radii are shown below.

Ion	Na^+	K^+	Rb^+	Cl^-	Br^-	I^-
Radius / pm	95	133	148	181	195	216

Predict the order of melting points for NaBr, KI and RbCl from lowest to highest.

Explain your answer.

Lowest melting point .....

.....

Highest melting point .....

Explanation .....

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[3]

[Total: 10]

Turn over

2 This question looks at different aspects of entropy.

(a) Three processes are given below.

For each process, state and explain whether the change would be accompanied by an increase or decrease in entropy.

(i) The freezing of water.

increase or decrease .....

explanation .....

.....

[1]

(ii) The reaction of calcium carbonate with hydrochloric acid.

increase or decrease .....

explanation .....

.....

[1]

(iii) The formation of $O_3(g)$ from $O_2(g)$.

increase or decrease .....

explanation .....

.....

[1]

(b) The enthalpy and entropy changes of a reaction both have a negative sign.

Discuss how the feasibility of this reaction will change as the temperature increases.

.....

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..... **[2]**

(c) The metal tungsten is obtained on a large scale from its main ore, wolframite. Wolframite contains tungsten(VI) oxide, WO_3.

Tungsten is extracted from wolframite by reduction with hydrogen:

$$WO_3(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(g) \qquad \Delta H = +115\,kJ\,mol^{-1}$$

Standard entropies are given in the table below.

Substance	$WO_3(s)$	$H_2(g)$	W(s)	$H_2O(g)$
$\boldsymbol{S^{\ominus}}$ **/ J K^{-1} mol^{-1}**	76	131	33	189

(i) Calculate the free energy change, ΔG, in kJ mol^{-1}, for this reaction at 25 °C.

Show your working.

ΔG at 25 °C = ... kJ mol^{-1} **[2]**

(ii) Calculate the minimum temperature, in K, at which this reaction becomes feasible.

Show your working.

minimum temperature = ... K **[2]**

[Total: 9]

Turn over

3 Ethyne gas, C_2H_2, is manufactured in large quantities for a variety of uses.

Much of this ethyne is manufactured from methane as shown in the equation below.

$$2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g) \qquad \Delta H = +377\,kJ\,mol^{-1}$$

(a) Write an expression for K_c for this equilibrium.

[1]

(b) A research chemist investigates how to improve the synthesis of ethyne from methane at a high temperature.

- The chemist adds CH_4 to a $4.00\,dm^3$ container.
- The chemist heats the container and allows equilibrium to be reached at constant temperature. The total gas volume does not change.
- The equilibrium mixture contains 9.36×10^{-2} mol CH_4 and 0.168 mol C_2H_2.

(i) Calculate the amount, in mol, of H_2 in the equilibrium mixture.

amount of H_2 = ... mol **[1]**

(ii) Calculate the equilibrium constant, K_c, at this temperature, including units.

Give your answer to **three** significant figures.

K_c = ... units .....**[3]**

(iii) Calculate the amount, in mol, of CH_4 that the chemist originally added to the container.

amount of CH_4 = ... mol **[1]**

(c) The chemist repeats the experiment three times.
In each experiment the chemist makes **one** change but uses the **same** initial amount of CH_4.

Complete the table to show the predicted effect of each change compared with the original experiment.

Only use the words **greater**, **smaller** or **same**.

Change	**K_c**	**Equilibrium amount of $C_2H_2(g)$ / mol**	**Initial rate**
The container is heated at constant pressure			
A smaller container is used			
A catalyst is added to CH_4 at the start			

[3]

(d) In this manufacture of ethyne, hydrogen is also produced. To improve the atom economy of the process, it is important to make use of the hydrogen. For example, hydrogen can be used in the extraction of some metals from their ores.

State **two** other large-scale uses of the hydrogen.

1 .....

2 .....

[1]

[Total: 10]

4 A student carries out an initial rates investigation on the reaction below.

$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

From the results, the student determines the rate equation for this reaction:

$$\text{rate} = k\,[I^-(aq)]^2\,[IO_3^-(aq)]\,[H^+(aq)]^2$$

(a) (i) What is the overall order of reaction?

..... **[1]**

(ii) A proposed mechanism for this reaction takes place in several steps.

Suggest **two** reasons why it is unlikely that this reaction could take place in one step.

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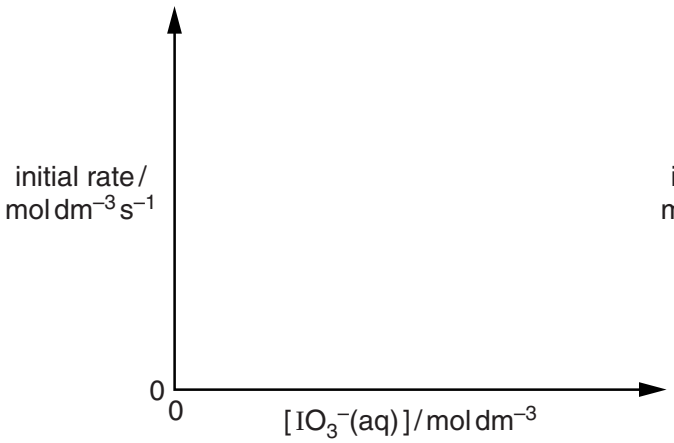
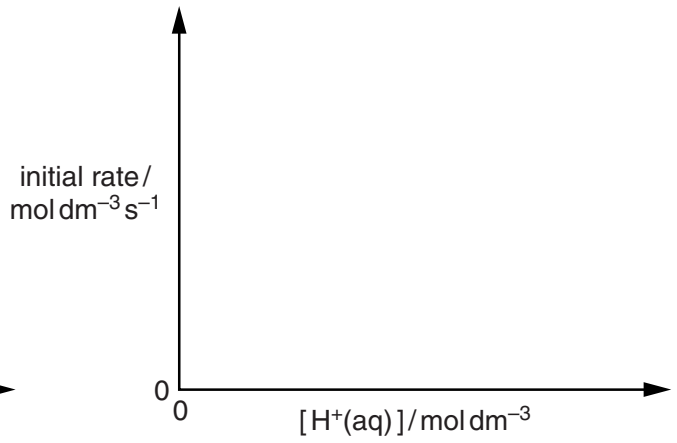
..... **[2]**

(b) On the rate–concentration graphs below, sketch lines to show the relationship between initial rate and concentration for $IO_3^-(aq)$ and $H^+(aq)$.





[2]

(c) The table below shows some of the student's results.

(i) Complete the table by adding the missing initial rates in the boxes.

	$[I^-(aq)]$ / mol dm^{-3}	**$[IO_3^-(aq)]$ / mol dm^{-3}**	**$[H^+(aq)]$ / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
Experiment 1	0.015	0.010	0.020	0.60
Experiment 2	0.045	0.010	0.020	
Experiment 3	0.060	0.040	0.080	

[2]

(ii) Calculate the rate constant, *k*, for this reaction. Include units.

Give your answer to **two** significant figures.

k = ... units .....**[3]**

(iii) The student repeats Experiment 1 using 0.020 mol dm^{-3} methanoic acid, HCOOH(aq) (pK_a = 3.75), instead of 0.020 mol dm^{-3} HC*l*(aq) as a source of H^+(aq).

Determine the initial rate in this experiment. Show your working.

initial rate = ... mol dm^{-3} s^{-1} **[3]**

[Total: 13]

Turn over

5 Elements in the d-block of the Periodic Table form ions that combine with ligands to form complex ions. Most d-block elements are also classified as transition elements.

(a) Explain why two of the Period 4 d-block elements (Sc–Zn) are **not** also transition elements.

In your answer you should link full electron configurations to your explanations.

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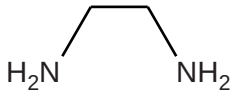
..... **[6]**

(b) The cobalt(III) ion, Co^{3+}, forms a complex ion **A** with two chloride ligands and two ethanediamine, $H_2NCH_2CH_2NH_2$, ligands.

The structure of ethanediamine is shown below.



(i) Explain how ethanediamine is able to act as a bidentate ligand.

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..... **[2]**

(ii) Write the formula of complex ion **A**.

..... **[1]**

(iii) What is the coordination number of cobalt in complex ion **A**?

..... **[1]**

(iv) Complex ion **A** has *cis* and *trans* stereoisomers. One of these stereoisomers also has an optical isomer.

Draw 3-D diagrams to show the three stereoisomers.

[3]

Question 5 continues on page 12

(c) The equilibrium reaction for the transport of oxygen by haemoglobin (Hb) in blood can be represented as **equation 5.1**.

$$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq) \qquad \textbf{equation 5.1}$$

(i) Explain how ligand substitution reactions allow haemoglobin to transport oxygen in blood.

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.....

..... **[2]**

(ii) Write an expression for the stability constant, K_{stab}, for the equilibrium involved in the transport of oxygen by haemoglobin.

Use the simplified species in **equation 5.1**.

[1]

(iii) In the presence of carbon monoxide, less oxygen is transported in the blood.

Suggest why, in terms of bond strength and stability constants.

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..... **[2]**

[Total: 18]

6 Ethanoic acid, CH_3COOH, is a weak Brønsted–Lowry acid.

(a) An acid–base equilibrium is set up when ethanoic acid is added to water.

Write the equation for the equilibrium that would be set up and label the two conjugate acid–base pairs.

..... + ... $\rightleftharpoons$ ..... + ...

....

[2]

(b) An aqueous solution of CH_3COOH has a pH of 3.060.
This solution contains both hydrogen ions and hydroxide ions.

(i) How can an aqueous solution of an acid contain hydroxide ions?

.....

..... **[1]**

(ii) Calculate the concentration of hydroxide ions in this solution of ethanoic acid.

concentration of hydroxide ions = ... $mol\,dm^{-3}$ **[2]**

Turn over

(c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate.
The resulting solution is able to act as a buffer solution.

(i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.

..... **[1]**

(ii) Explain why this buffer solution has formed.

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..... **[1]**

(iii) Explain how this buffer solution controls pH when either an acid or an alkali is added.

In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

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..... **[5]**

(d) A biochemist plans to make up a buffer solution with a pH of 5.000.
The biochemist adds solid sodium ethanoate, CH_3COONa, to 400 cm^3 of 0.200 $mol\,dm^{-3}$ ethanoic acid.
K_a for ethanoic acid = $1.75 \times 10^{-5}\,mol\,dm^{-3}$

Calculate the mass of sodium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

Assume that the volume of the solution remains constant at 400 cm^3 on dissolving the sodium ethanoate.

[5]

[Total: 17]

Turn over

7 Electrochemical cells contain two redox systems, one providing electrons and the other accepting electrons. The tendency to lose or gain electrons is measured using values called standard electrode potentials.

(a) Define the term *standard electrode potential*.

Include all standard conditions in your answer.

.....

.....

.....

..... **[2]**

(b) The table below shows two redox systems and their standard electrode potentials, $E^{\ominus}$.

Redox system	$E^{\ominus}$ **/ V**
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Ag^{+}(aq) + e^- \rightleftharpoons Ag(s)$	+0.80

A standard $Cu^{2+}(aq)/Cu(s)$ half-cell is connected to a standard $Ag^{+}(aq)/Ag(s)$ half-cell. The potential of the cell is measured.

Water is then added to the $Cu^{2+}(aq)/Cu(s)$ half-cell. This changes the position of equilibrium in the half-cell. The cell potential increases.

(i) Write down the equation for the overall cell reaction.

..... **[1]**

(ii) Explain, in terms of equilibrium, why the cell potential increases.

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.....

..... **[3]**

(c) Hydrogen fuel cells are being developed for powering vehicles.

(i) State **one** advantage of using hydrogen as a fuel compared with conventional fuels.

.....

..... **[1]**

(ii) In vehicles, hydrogen can be stored on the surface of a solid material or within a solid material.

State **one** other way that hydrogen can be stored as a fuel for vehicles.

.....

..... **[1]**

(d) Aluminium–oxygen cells are being investigated for powering vehicles.

The **reactions** at each electrode are shown below.

$$Al(s) + 4OH^-(aq) \longrightarrow Al(OH)_4^-(aq) + 3e^-$$

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

(i) The standard electrode potential for the O_2/OH^- redox system is +0.40V.
The standard cell potential of an aluminium–oxygen cell is 2.71V.

What is the standard electrode potential of the aluminium redox system in this cell?

standard electrode potential = ... V **[1]**

(ii) Construct the overall cell equation for an aluminium–oxygen cell.

[2]

[Total: 11]

8 A student carries out an investigation to prepare and analyse a sample of barium ferrate(VI), $BaFeO_4$. The steps in the investigation are shown below.

Step 1

The student adds solid iron(III) oxide to a hot aqueous solution containing an excess of hydroxide ions. The student bubbles chlorine gas through the mixture.
A solution forms containing aqueous ferrate(VI) ions, $FeO_4^{2-}(aq)$, and aqueous chloride ions.

Step 2

The student adds aqueous barium chloride to the resulting solution.
A precipitate of impure barium ferrate(VI) forms.
The precipitate is filtered, washed with distilled water and dried.
The student obtains 0.437 g of impure solid barium ferrate(VI).

Step 3

An excess of acidified aqueous potassium iodide is added to the solid from **step 2**.
The $BaFeO_4$ reacts as shown below, and the impurity does not react. A solution forms containing aqueous iodine, $I_2(aq)$.

$$BaFeO_4(s) + 8H^+(aq) + 3I^-(aq) \longrightarrow Fe^{3+}(aq) + Ba^{2+}(aq) + 1\tfrac{1}{2}I_2(aq) + 4H_2O(l)$$

Step 4

The student determines the amount of I_2 formed by carrying out a titration with aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

26.4 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3(aq)$ are required to reach the end point.

(a) Construct an equation for the oxidation of iron(III) oxide (**step 1**).

..... **[2]**

(b) Write an **ionic** equation for the formation of barium ferrate(VI) (**step 2**).

Include state symbols.

..... **[1]**

(c) In **step 3**, what is the reducing agent?

Explain your answer in terms of electrons.

reducing agent .....

explanation .....

.....

.....

[2]

(d) The solid sample of barium ferrate(VI) obtained in step 2 is impure.

Determine the percentage, by mass, of barium ferrate(VI) in the 0.437 g of solid formed in **step 2**.

Give your answer to **one** decimal place.

percentage of barium ferrate(VI) = ... % **[4]**

Question 8 continues on page 20

(e) When the solution is not alkaline, ferrate(VI) ions react with water.
The reaction forms a gas with a density of 1.333×10^{-3} g cm^{-3}, measured at room temperature and pressure, and an orange–brown precipitate.

- Determine the formulae of the gas and the precipitate.
- Write an equation for the reaction that takes place.

gas .....

precipitate .....

equation

.....

[3]

[Total: 12]

END OF QUESTION PAPER