### Answer **all** the questions

### 1 Planning (P)

Iron(II) sulfate is one of the most readily available sources of iron(II). Hence it is used to make iron supplement tablets to treat anaemia and other iron deficiencies. Women are at a higher risk for iron-deficiency anaemia than men, especially pregnant women. However, excess iron in the body can lead to health problems, and in severe cases, death.

The percentage by mass of iron in an iron supplement tablet can be determined by titrating it with acidified potassium manganate(VII).

(a) Using the Data Booklet, write an ionic equation for the reaction between iron(II) sulfate and acidified potassium manganate(VII).

[1]

(b) If the concentration of a standard solution of potassium manganate(VII) is 0.500 mol dm<sup>-3</sup>, calculate the range of mass of powdered iron supplement tablets needed for a suitable and reliable titration. You may assume that the percentage mass of iron in iron supplement tablets is between 80% to 90%. 1 (c) Write a plan for the titration that you would carry out to calculate the mass of iron present in the tablet. You are given a 0.500 mol dm<sup>-3</sup> standard solution of potassium manganate(VII) and excess powdered iron tablets. You may use the reagents and apparatus normally found in a school or college laboratory.

In your plan, you should give:

Details, including quantities of all reagents and capacities of apparatus used; The essential details of the titration procedure.



d) Some women take multi-vitamin pills to supplement their diet which often also contain mineral ions such as Cu<sup>2+</sup>. However, too much Cu<sup>2+</sup> in our body causes various health problems. In a manufacturing error, a batch of multi-vitamin pills contained too much Cu<sup>2+</sup> and was also contaminated accidentally with a small amount of Ba<sup>2+</sup> ions which are poisonous.

A sample from this batch of multi-vitamin pills is dissolved to form a solution. You are to devise a series of chemical tests which can be conducted under laboratory conditions using common laboratory reagents and apparatus to separate the two cations above, such that each cation is present in a separate precipitate.

Test	Expected observation	Identity of cation in
		precipitate

Record your plan in the table below.

# [3] [Total: 12 marks]

- **2** Phosphorus tribromide is a colourless liquid that is commonly used in laboratories for the manufacture of alkyl bromide from alcohols.
  - (a) (i) Draw a dot and cross diagram of phosphorus tribromide.

(ii) Draw the structure for the compound formed when phosphorus tribromide reacts with boron tribromide

(iii) Suggest whether phosphorus tribromide or boron tribromide has a higher boiling point. Explain.

(b) Phosphorus tribromide reacts in a similar way as phosphorus trichloride.Write an equation, with state symbols, to show the reaction of phosphorus tribromide with water.

[5]

2 (c) Using the information from the table below and any relevant data from the *Data Booklet*, construct an energy level diagram to calculate the bond energy of the P-Br bond.

						∆H/ kJmol <sup>-1</sup>
Atomisation energy of phosphorus			+315			
Enthalpy change of formation of phosphorus tribromide			-185			
Enthalpy cl tribromide	hange	of	vapourisation	of	phosphorus	+39

[4]

2 (d) The general equation for the formation of alkyl bromide from alcohols using phosphorus tribromide is:

 $PBr_3 + 3ROH \rightarrow 3RBr + H_3PO_3$ 

The reaction mechanism for the above reaction using ethanol and phosphorus tribromide is shown below.



- (i) State the type of reaction for the overall reaction
- (ii) Complete the mechanism above by using partial charges, lone pairs and curly arrows to represent the electron flow.
- (iii) Suggest a reason why this reaction method cannot be used to prepare C(CH<sub>3</sub>)<sub>3</sub>Br.

(iv) Using the above mechanism in 2(d), suggest the organic compound formed when ethanoic acid is reacted with phosphorus tribromide.



2 (e) PBr<sub>3</sub> is used in the following reaction scheme to produce a sweet-smelling compound **D**.

(i) Draw the structures of **A** to **D** in the spaces provided above.

2 (e) (ii) Give the reagents and conditions for Steps II, III, IV and VI.

Step II: _	
Step III:	
Step IV:	
Step VI:	

[8] [Total: 25 marks]

**3** Hydrogen peroxide exhibits oxidising and reducing properties, depending on pH.

In acidic solutions,  $H_2O_2$  is one of the most powerful oxidising agents known and is used commonly as a bleaching agent and disinfectant.

In one of its reactions, it oxidises potassium iodide to form iodine and water.

(a) With reference to the Data Booklet, write the balanced equation for the reaction between hydrogen peroxide and potassium iodide.

[1]

(b) To study the kinetics of the above reaction, two sets of separate experiments were performed, in which the initial concentrations of each of the reactants were varied in turn, the other two being kept constant. The results are shown below.



**W**:  $[H_2O_2] = 1.0 \text{ mol } dm^{-3} \text{ and } [I^-] = 1.0 \text{ mol } dm^{-3}$ **X**:  $[H_2O_2] = 2.0 \text{ mol } dm^{-3} \text{ and } [I^-] = 1.0 \text{ mol } dm^{-3}$ **Y**:  $[H_2O_2] = 1.0 \text{ mol } dm^{-3} \text{ and } [H^+] = 1.0 \text{ mol } dm^{-3}$ **Z**:  $[H_2O_2] = 2.0 \text{ mol } dm^{-3} \text{ and } [H^+] = 1.0 \text{ mol } dm^{-3}$ 

Use the data above to deduce the rate equation and give the units for the rate constant.

9

3

3 (c) Two different mechanisms have been proposed for this reaction.

Mechanism A:

 $\begin{array}{ll} H_2O_2+I^- \xrightarrow{} H_2O+OI^- & (slow) \\ OI^- +H^+ \xrightarrow{} HOI & (fast) \\ HOI+H^+ +I^- \xrightarrow{} I_2+H_2O & (fast) \end{array}$ 

Mechanism B:

 $\begin{array}{ll} H_2O_2+I^{\scriptscriptstyle -}+H^{\scriptscriptstyle +} \rightarrow H_2O+HIO & (slow) \\ HIO+I^{\scriptscriptstyle -} \rightarrow I_2+OH^{\scriptscriptstyle -} & (fast) \\ OH^{\scriptscriptstyle -}+H^{\scriptscriptstyle +} \rightarrow H_2O & (fast) \end{array}$ 

Suggest with reasons which of the two mechanisms, **A** or **B**, fits the kinetic data in (b).

[2]

(d) Draw the energy profile diagram for the reaction based on mechanism A.

10

- 4 Cobalt has been used for centuries to impart a rich blue color to glass and ceramics.
  - (a) A complex of cobalt is prepared by the following method: Air is bubbled through an aqueous solution containing CoCl<sub>2</sub>, NH<sub>3</sub> and NH<sub>4</sub>Cl. The resulting solution was evaporated and crystals of the cobalt compound, P can be isolated. P has an octahedral cation, and is found to have the following composition by mass: Co: 25.2%; N: 24.0%; H: 5.1%; Cl: 45.7%
    - (i) Given the molar mass of P is 233.4, calculate the molecular formula of P and suggest the ligands that are bonded to cobalt.

(ii) On adding an excess of aqueous solution of silver nitrate to an aqueous solution of 0.01 mol of P, 1.43 g of silver chloride is precipitated.
 Given that P has no overall dipole moment, deduce the structural formula of P. Draw the full structure of its cation, showing clearly the arrangement of the ligands that surround cobalt.

[Turn over

**4** (b) A student carried out the following experiment in the laboratory to investigate the chemistry of cobalt compounds.

### Procedures

Step 1	5 g of the potassium sodium tartrate was weighed into a
	250 cm <sup>3</sup> beaker. 60 cm <sup>3</sup> of distilled water was added and the solution
	was stirred.
Step 2	20 cm <sup>3</sup> of hydrogen peroxide solution was added to the solution in
	step 1.

Effervescence was observed after 5 hours.

The student repeated the experiment with the addition of 2 cm<sup>3</sup> of cobalt(II) chloride solution to the mixture. He recorded the following observations:

The solution in the beaker turned from colourless to pink when cobalt(II) chloride solution was added. The solution then turned green and vigorous effervescence was observed immediately. When the effervescence stopped, the solution turned back to pink.

What was the role of cobalt(II) chloride solution in the experiment? Give two reasons to support your answer using the information above.

**4** (c) When a crystal of NH₄SCN was added to cobalt(II) chloride solution, the solution changed colour and the visible absorption spectrum for the resulting solution was shown below:



White light spectrum

	red	gree	en blue	violet
Wavelength(nm)	700 6	00 500	400	300

(i) What is the colour of the resulting solution?

(ii) Explain why the resulting solution is coloured.

## [4] [Total: 13marks]

- 5 This question involves various cyclic compounds and their reactions.
  - (a) In the Shapiro reaction, a carbonyl group reacts in the presence of an electrophile to form an alkene. A simplified example of the Shapiro reaction is shown below.



where E represents an electrophile

Shapiro reaction is used on **Q**.



- (i) State the number of chiral centers in Q
  Number of chiral centers = \_\_\_\_\_\_
- (ii) In the diagram below, circle the  $sp^2$  hybridised carbons.



5 (a) (iii) Draw the structures of the product formed when Q reacts with each of the following reagents in the Shapiro reaction.

H <sub>2</sub> O	Chloroethane
-	

(iv) Cyclic esters R and S are possible products of the Shapiro reaction.



Suggest reagents and conditions to distinguish between esters **R** and **S**. State the observations for each ester.

Reagents and conditions:

Observations:

(b) The structure of a dicarboxylic acid **J** is shown below.



(i) The pKa values of the two acidic groups in J are 2.2 and 6.4. In the diagram above, circle the acidic group which has a pKa value of 2.2. Explain your answer.

K is an isomer of J.



(ii) State the type of isomerism exhibited in J and K.

5 (b) (iii) With the aid of a diagram, explain why J has a more stable mono-anion than the mono-anion of K.

[5] [Total: 11 marks]

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