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 **11** printed pages.

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1 **(a)** Cadmium sulfide (CdS) is a toxic yellow pigment. Some data concerning CdS is printed below.

K_{sp} at 298 K = 1.00×10^{-28}
Melting point: 2020 K

(i) Explain why CdS has a high melting point. [2]

(ii) Calculate the solubility, in grams per cubic decimeters, of CdS at 298 K. [2]

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(b) The aqua Cd^{2+} ion, represented as $Cd(H_2O)_6^{2+}$ shows acidic properties in water. The pK_a of this ion is 10.1.

(i) Calculate the pH of a solution of 0.100 mol dm^{-3} of $CdCl_2$. [2]

(ii) $Cd(CH_3CO_2)_2$, cadmium ethanoate, is soluble in water too. Compare the pH of a solution of cadmium ethanoate of the same concentration to that in **(i)**. [2]

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(c) Although cadmium sulfide has poor solubility in water, its solubility was observed to have increased significantly when CdS is dissolved in a solution of hydrochloric acid.

Explain this observation using acid-base equilibria. [2]

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[Total: 10]

2 (a) Volhard's method is a common method used to determine the concentration of chloride ions in a given solution.

A contaminated sample **X** contains sodium chloride and sodium carbonate, and other unknown impurities.

Part 1: Determination of percentage mass of sodium carbonate

0.500 grams of **X** was dissolved in water and made up to a 250 cm^3 solution.

25.0 cm^3 of solution was withdrawn into a conical flask, and titrated against a standard solution of 0.0500 mol dm^{-3} hydrochloric acid, with the indicator being methyl orange.

Some data concerning carbonic acid, H_2CO_3, is shown below:

pK_1 = 6.35
pK_2 = 10.33

The results were tabulated as follows:

Titre no.	1	2
Volume of HC*l* used / cm^3	15.30	15.40

In the titrations, 3 reactions took place regarding sodium carbonate.

Reaction 1: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$
Reaction 2: $HCO_3^- + H^+ \rightarrow H_2CO_3$
Reaction 3: $H_2CO_3 \rightleftharpoons CO_2 + H_2O$

(i) Calculate, by percentage of mass, the purity of sodium carbonate in **X**. [2]

(ii) Hence, sketch a graph of pH of the solution against volume of HC*l* added. [4]

You should include all pH values of vital points where they are possible to calculate.

(iii) State an essential assumption you made in your calculations. [1]

(iv) Phenolphthalein is also a suitable indicator that can be used for this titration. However, this indicator only detects the endpoint of **Reaction 1**.

Suggest why phenolphthalein isn't used as an indicator. [1]

(v) Explain why carbon dioxide was only produced in the later half of the titration. [1]

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(b) When aluminium chloride is added to a solution of sample **X**, effervescence was observed. A white precipitate of aluminium hydroxide is observed too.

The pK_a value of the aluminium ion is 4.27.

(i) Explain, with appropriate pK_a values, why aluminium hydroxide is the product. [2]

(ii) Explain **qualitatively** why aluminium carbonate is a very unstable salt. [2]

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(c) <u>Part 2: Determination of the amount of sodium chloride by the Volhard Method</u>

25.0 cm^3 of the solution in the volumetric flask in Part 1 was pipetted into a conical flask. 10.00 cm^3 of 0.100 mol dm^{-3} of hydrochloric acid was added.

25.0 cm^3 of 0.100 mol dm^{-3} of silver nitrate was then added into the conical flask. The resultant solution was then filtered, and the filtrate was collected. 0.100 cm^3 of 0.100 mol dm^{-3} iron(III) nitrate was then added to the filtrate.

The filtrate was then titrated against 0.0100 mol dm^{-3} of potassium thiocyanate (KSCN). At the endpoint, the solution turns slightly red, due to the formation of the iron(III) thiocyanate complex ion, $Fe(SCN)^{2+}$.

The average titre value obtained is 23.40 cm^3.

Some data is provided below:
K_{sp} (AgC*l*) = 2.02×10^{-10}
K_{sp} (AgSCN) = 1.03×10^{-12}

(i) The Volhard method needs to be conducted in an acidic environment. Show that an acidic environment has been established. [1]

(ii) Calculate the percentage by mass of sodium chloride in **X**. [3]

(iii) Explain, using the data provided, why it is advisable to filter off the silver chloride precipitate before commencing the precipitation titration like that in the description. [1]

(iv) The silver chloride precipitate can be dissolved in aqueous ammonia. Explain how so. [2]

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(d) Mohr's method is another way to determine the concentration of chloride ions in a solution.

A 25.0 cm^3 of 0.100 mol dm^{-3} sodium chloride solution was titrated against 0.100 mol dm^{-3} silver nitrate solution. Before the titration, 0.100 cm^3 of 0.100 mol dm^{-3} of K_2CrO_4 was added. At the endpoint, a slight orange precipitate (Ag_2CrO_4) is formed.

K_{sp} (Ag_2CrO_4) = 3.01×10^{-12}

(i) Given that the volume of titrant needed to reach the endpoint is 25.0 cm^3, find the concentration of Ag^+ present in the solution at the endpoint. [1]

(ii) Hence, calculate the percentage of chloride ions that have precipitated out at the endpoint to 2 decimal places, and comment on whether Mohr's method is a good method to accurately determine the concentration of chloride ions. [2]

(iii) Explain why AgC*l* precipitates first before Ag_2CrO_4. [1]

(iv) Explain if this method can be used if an unknown concentration of sulfate ions had to be determined instead. [1]

K_{sp} (Ag_2SO_4) = 1.20×10^{-5}

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[Total: 25]