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.

---

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]

B1 – Structure and bonding
CdS has a giant ionic lattice where oppositely charged Cd^{2+} and S^{2-} ions held by strong electrostatic attraction.

B1 – Explains high melting point
Because this electrostatic attraction is strong, it takes a large amount of heat to break the ionic bonds, hence the high melting point.

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

M1 – Calculates solubility in mol dm^{-3}
Solubility = $\sqrt{1.00 \times 10^{-28}} = 1.00 \times 10^{-14}$ mol dm^{-3}

MA1 – Correct answer
In grams per cubic decimeters: $1.00 \times 10^{-14} \times (112.4 + 32.1) = 1.45 \times 10^{-12}$ g dm^{-3}

(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]

M1 – Correct equation in terms of [H+]

$$\frac{[H^+]^2}{0.100 - [H^+]} = 10^{-10.1}$$

MA1 – Correct answer with working

$[H^+] = 0.00000281834 \text{ mol dm}^{-3}$
$pH = -\log_{10}[H^+] = 5.55$

(The quadratic equation can be solved with your scientific calculator)
Note: If you use an approximation, you need to write:
Assume that $[H^+] << 0.100 \text{ mol dm}^{-3}$
before the subsequent manipulations you carry out

There's no method mark for how you solve the quadratic equation (because this isn't a H2 Math paper), just give the marker the correct $[H^+]$.

(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]

B1 – Higher for the ethanoate
B1 – Idea of a conjugate acid-base reaction lowering $[H^+]$
Some of the ethanoate ions will reassociate with free protons to form ethanoic acid molecules CH_3CO_2H, lowering the concentration of $[H^+]$ which increases the pH.

(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]

B1 – Relevant equations (or worded descriptions in the explanation)

$$H^+ + S^{2-} \rightleftharpoons HS^- \text{ -- (1)}$$
$$CdS \rightleftharpoons Cd^{2+} + S^{2-} \text{ -- (2)}$$

B1 – Accompanying explanations
A high concentration of H^+ causes the position of equilibrium (1) to shift right, thereby lowering the concentration of sulfide ions.
Subsequently the position of equilibrium (2) shifts right (to compensate for the decrease in concentration of sulfide ions), thus more CdS dissolves, increasing its solubility.

If you feel that equations aid your explanation, feel free to write them because you are giving yourself more chances to score!

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]

M1 – Calculates total number of moles of CO_3^{2-}

$$n_{CO_3^{2-}}\text{(total)} = \frac{15.35}{1000} \times 0.0500 \times \frac{1}{2} \times \frac{250}{25.0} = 0.0038375\text{ mol}$$

MA1 – Final working leading to correct answer

$$\text{purity} = \frac{0.0038375 \times (2 \times 23.0 + 12.0 + 16.0 \times 3)}{0.500} \times 100\% = 81.4\%$$

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

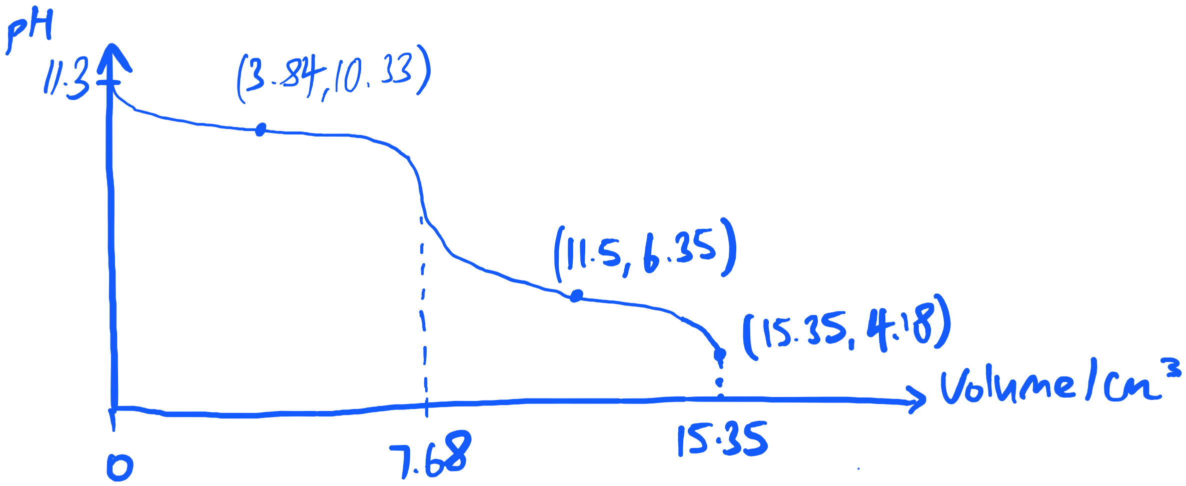
You should include all pH values of vital points where they are possible to calculate.

B2 – Correct pH values at critical points (award 0.5 pts for 1 correct)

Volume / cm^3	pH	Working (not required)
0	11.3	$[CO_3^{2-}] = 0.01535$ mol dm^{-3} $[OH^-] = \sqrt{0.01535\times10^{-(14-10.33)}} = 0.001812$ mol dm^{-3} pH = 14 + $\log_{10}(0.001812) = 11.3$
3.84 (or 3.85)	10.33	
11.51 (or 11.5 to 3 sf)	6.35	
15.35	4.18	$[H_2CO_3] = 0.01535 \times \frac{25.0}{25.0+15.35} = 0.0095105$ mol dm^{-3} $[H^+] = \sqrt{10^{-6.33} \times 0.0095105} = 6.67 \times 10^{-5}$ mol dm^{-3} pH = $-\log_{10}(6.67 \times 10^{-5}) = 4.18$

Due to the low mark allocation for the pH values, you may just approximate the pH without justification as shown above.

B1 – Correct axes and labels
B1 – Correct shape of graph



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

B1 – No other substances in X has acid-base properties that can alter the pH of the solution.

(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]

B1 – The titre value will be around 7.70 cm^3 which is too low due to a high percentage error of the data.

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

B1 - The first protonation will inevitably take place first since the carbonate ion is a stronger base than the hydrogencarbonate ion.

It's only during the second protonation where carbonic acid is formed where carbon dioxide can be produced.

(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]

B1 – Compares pK_a values to derive the conclusion that an acid base reaction will occur

Because the pK_a value of the aluminium ion (4.27) is less than both the pK_a values of carbonic acid (6.35 and 10.33), an acid base reaction between the aluminium ion and carbonate ion will occur.

B1 – Explains formation of product

3 successive deprotonations of the aqua-aluminium ion occurs to yield aluminium hydroxide.

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

B1 – The aluminium ion has a high polarising power because of its high charge of 3+ but low ionic radius.

B1 – The high polarising power causes severe distortion of the electron cloud of the carbonate ion, weakening the C—O bonds which causes the carbonate ion to be unstable and hence the salt is very unstable.

(c) **Part 2: Determination of the amount of sodium chloride by the Volhard Method**

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]

B1 – Supports answer with relevant calculations

$$n_{H^+} \text{ to neutralise } CO_3^{2-} \text{ ions (in (a))} = \frac{15.35}{1000} \times 0.0500 = 0.0007675 \text{ mol}$$

But

$$n_{H^+} \text{ to neutralise } CO_3^{2-} \text{ ions (in (c))} = \frac{10.0}{1000} \times 0.100 = 0.00100 \text{ mol}$$

Hence more than enough acid is added in (c). So an acidic environment is established.

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

$$n_{\text{AgSCN}} = \frac{23.40}{1000} \times 0.0100 = 0.000234\, mol$$

M1 – Calculates how much chloride ions reacted with silver ions

$$n_{\text{Cl}^-}(\text{reacted with Ag}^+) = \frac{25.0}{1000} \times 0.100 - 0.000234 = 0.002266 \text{ mol}$$

M1 – Accounts for addition of HC*l*

$$n_{\text{Cl}^-}\left(\text{from NaCl in 25.0 cm}^3\text{ solution from Part 1}\right) = 0.002266 - \frac{10.0}{1000} \times 0.100$$
$$= 0.0001266 \text{ mol}$$

$$n_{\text{NaCl}}\ (\text{in } \mathbf{X}) = 0.0000160 \times \frac{250}{25.0} = 0.000160 \text{ mol}$$

MA1 – Final working to obtain correct answer

$$\%\ \text{NaC}l = \frac{0.001266 \times (23.0 + 35.5)}{0.500} \times 100\% = 14.8\%$$

(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]

B1 – Uses K_{sp} values to explain
K_{sp} (silver chloride) > K_{sp} (silver thiocyanate) → silver chloride is more soluble than silver thiocyanate
When thiocyanate ions are added past the endpoint when the solution is not filtered, it will displace the chloride ion in silver chloride and form additional AgSCN precipitate which leads to inaccurate results.

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

B1 – 2 equilibrium equations stated below (do not accept worded form)

$$\text{AgC}l \rightleftharpoons \text{Ag}^+ + \text{C}l^- \text{ -- (1)}$$
$$\text{Ag}^+ + 2\ \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)_2]^+ \text{ -- (2)}$$

B1 – An explanation based on equilibrium principles
Ammonia will form a soluble complex with silver ion via equation (2). Hence, this causes the concentration of Ag^+ to decrease. Hence, the position of equilibrium (1) shifts right and AgC*l* dissolves to form Ag^+ to compensate for the decrease in concentration of Ag^+.

(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]

MA1 – Correct deduction below, together with correct working
At the endpoint, Ag_2CrO_4 precipitate is about to form.

$$\left[CrO_4^{2-}\right] = \frac{0.100}{0.100 + 25.0 + 25.0} \times 0.100 = 0.0001996 \text{ mol dm}^{-3}$$

So since $[Ag^+]^2 [CrO_4^{2-}] = 3.01 \times 10^{-12}$

$$[Ag^+] = \sqrt{\frac{3.01 \times 10^{-12}}{0.0001996}} = 0.0001228 = 0.000123 \text{ mol dm}^{-3}$$

(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]

MA1 – The below

$$n_{Ag^+}(\text{not precipitated}) = 0.0001228 \times \frac{25.0 + 25.0 + 0.100}{1000} = 0.000006152 \text{ mol}$$

$$n_{Ag^+}(\text{start}) = \frac{25.0}{1000} \times 0.100 = 0.00250 \text{ mol}$$

So percentage of chloride ions precipitated out (which is percentage of silver ions precipitated out) is,

$$\frac{0.00250 - 0.000006152}{0.00250} \times 100\% = 99.75\%$$

B1 – Good test because almost close to 100% of chloride ions are precipitated.

(iii) Explain why $AgCl$ precipitates first before Ag_2CrO_4. [1]

B1 – Lower solubility of $AgCl$ in water compared to Ag_2CrO_4. (No need for calculation)

(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}

B1 – It cannot be used because silver sulfate has a higher solubility than that of silver chromate(VI) since K_{sp} $(Ag_2SO_4) > K_{sp}$ (Ag_2CrO_4), so silver chromate will precipitate out first before silver sulfate does, rendering the indicator useless and there will be no clear endpoint.