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.

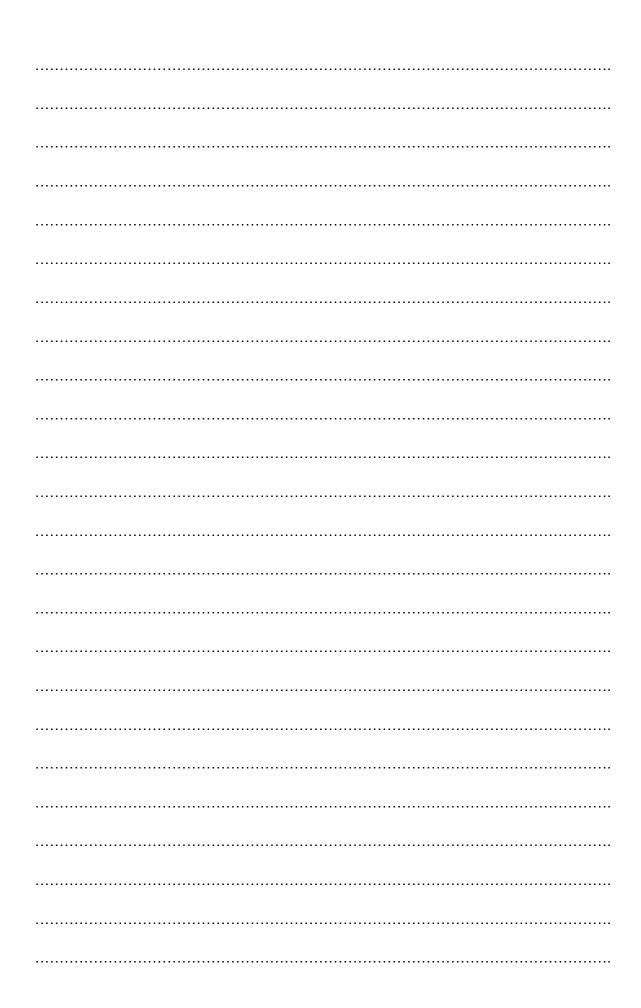This document consists a total of **12** printed pages.

---

1 (a) The molar volume of a gas at room temperature and pressure is 24 dm^3 mol^{-1}.

    (i) Define the *mole*. [1]

    (ii) Derive the quantity stated in **(a)**. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(b) An essential assumption you had to use in part **(a)(ii)** was that the gas was ideal.

(i) State 3 assumptions of an ideal gas. [2]

(ii) A real gas is not ideal, but can behave as an ideal gas under certain conditions. State these conditions and explain why so. [2]
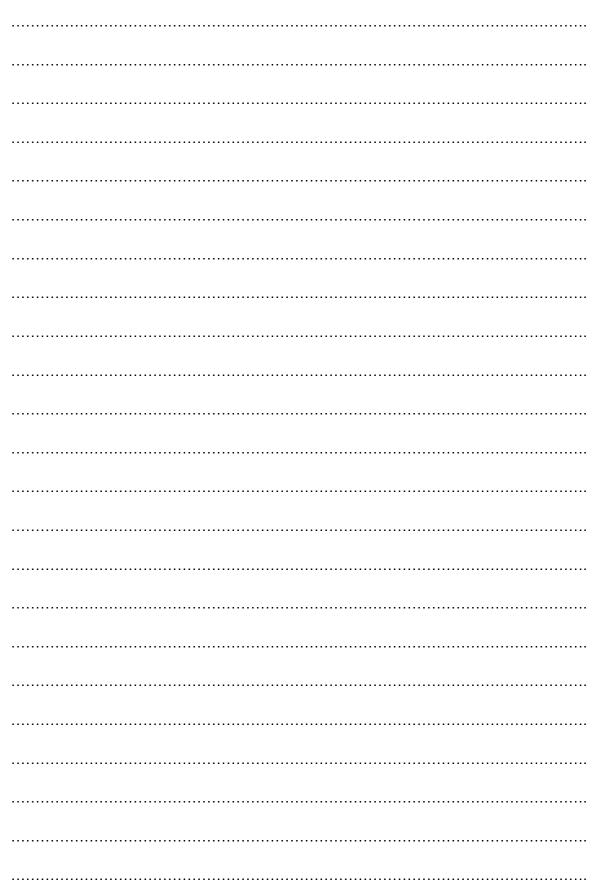
....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(c) Tin is a Group IV element. It forms a mixed oxide, **F**, that contains the metal in both oxidation states II and IV. The formula of **F** can be found by the following method.
A sample of **F** was dissolved in H_2SO_4 (aq), producing solution **G**, which was a mixture of tin(II) sulfate and tin(IV) sulfate.

A 25.0 cm^3 sample of solution **G** was titrated with 0.0200 mol dm^{-3} $KMnO_4$. 13.50 cm^3 of $KMnO_4$ was required to reach the end-point. The reaction occurring during the titration is

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \rightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(i) Calculate the amount in moles of Sn^{2+} in 25.0 cm^3 of solution **G**. [2]

Another 25.0 cm^3 sample of solution **G** was stirred with an excess of powdered zinc. This converted all the tin(IV) to tin(II). The excess zinc powder was filtered off and the filtrate was titrated with 0.0200 mol dm^{-3} $KMnO_4$ as before. This time, 20.30 cm^3 of $KMnO_4$ was required to reach the end-point.

(ii) Calculate the amount in moles of Sn^{4+} in 25.0 cm^3 of solution **G** and hence deduce the Sn^{2+}/Sn^{4+} ratio in the oxide **F**. [2]

(iii) Write the formulae for tin(II) oxide and tin(IV) oxide. [1]

(iv) Using your answers to **(c)(ii)** and **(c)(iii)**, suggest the formula of **F**. [1]

(v) Powdered iron can also convert all the tin(IV) in solution **G** to tin(II). In the process, the iron is oxidised to iron(II).

Explain how the second titre value would be affected if powdered iron was used in place of powdered zinc in the experiment. [1]

....

....

....

....

....

....

....

....

(d) On **separate** axes, sketch a graph showing the behaviour of an ideal gas, of

(i) **1** pV against p, with constant n and T.

2 density against T, with constant n and p.

3 p against $\frac{1}{V}$, with constant n and T. [4]

(ii) On the **same** axes of part **(d)(i)1**, sketch a graph showing the behaviour for
A N_2; and
B NH_3; with the conditions stated in **d(i)1**. [2]

Label the corresponding lines as **A** and **B**.

(iii) Account for the shape of your graph for **(d)(ii)A**. [2]

(iv) Account for the difference in the shape of your graph for **(d)(ii)A** and **B**. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 23]

2 Silicon is able to form highly coordinated compounds with electronegative elements such as fluorine. As metal fluorides are often used as fluorination reagents, highly coordinated silicon fluorides also act as fluorination reagents.

Part 1: Standardisation of Na_2SiF_6 solution

Aqueous solution **F**: 0.855 g of Na_2SiF_6 (M_r = 188.053) dissolved in water (total volume: 200 cm^3)
Aqueous solution **G**: 6.86 g of $Ce_2(SO_4)_3$ (M_r = 568.424) dissolved in water (total volume: 200 cm^3)

Precipitation titration of 50.0 cm^3 of solution **F** by dropwise adding solution **G** in the presence of xylenol orange, which coordinates to Ce^{3+}, as an indicator was conducted. After adding 18.8 cm^3 of solution **G**, the colour of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce^{3+}, and the only resulting silicon compound is $Si(OH)_4$. The endpoint is where no more precipitate is formed.
The precipitation reaction is not a redox reaction.

(a) (i) Calculate the amount of Na_2SiF_6 and $Ce_2(SO_4)_3$ reacted in this titration to 4 significant figures. [2]

(ii) Suggest the identity of the precipitate generated in this titration. [1]

(iii) Draw the dot-and-cross diagram for Na_2SiF_6. [1]

(iv) Suggest a chemical equation for the precipitation titration. [1]

………

………

………

………

………

………

………

………

………

………

Part 2: Reaction of CCl_4 with Na$_2$SiF$_6$

The fluorination reaction of CCl_4 using Na$_2$SiF$_6$ was carried out as follows.

CCl_4 reacts with Na$_2$SiF$_6$ to form a chlorofluorocarbon (CFC), of varying number of fluorine atoms in the product (1 to 4). NaCl is the by-product.

***x* grams** of Na$_2$SiF$_6$ were added to 500.0 g of CCl_4 and heated to 600 K in a sealed pressure-resistant reaction vessel. The unreacted Na$_2$SiF$_6$ and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 dm^3 with CCl_4 (solution **H**). Solution **H** only contains SiF$_4$ as a silicon-containing compound.

A ^{19}F NMR spectrum detects products CFCl_3, CF$_2$Cl_2, CF$_3$Cl, and CF$_4$ (Table 1).
The integration ratios in the ^{19}F NMR spectrum are proportional to the number of fluorine nuclei.

^{19}F NMR Data	CFCl_3	CF$_2$Cl_2	CF$_3$Cl	CF$_4$
Integration ratio	45.0	65.0	18.0	2.0

SiF$_4$ is hydrolysed to form H$_2$SiF$_6$ according to the following equation.

$$3\ SiF_4 + 2\ H_2O \rightarrow SiO_2 + 2\ H_2SiF_6$$

10.0 cm^3 of solution **H** was added to an excess amount of water, which resulted in the complete hydrolysis of SiF$_4$. After separation, the H$_2$SiF$_6$ generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na$_2$SiF$_6$ (aqueous solution **J**).

The precipitate of unreacted Na$_2$SiF$_6$ and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (named solution **K**; volume = 10.0 dm^3).

Then, additional precipitation titrations using solution **G** were carried out, and the endpoints of the titrations with **G** were as follows:
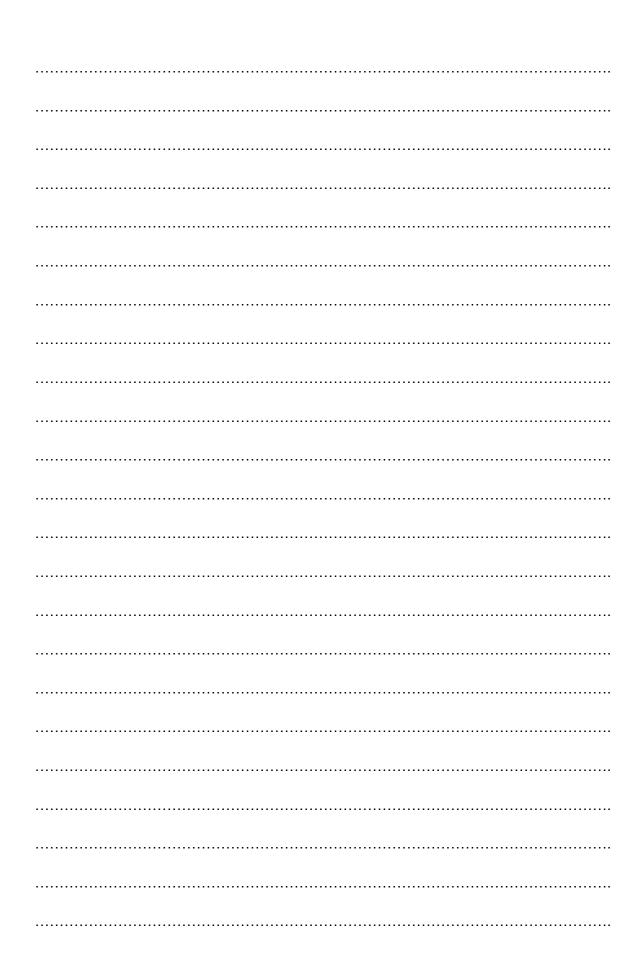
- For solution **J** (entire amount): 61.6 cm^3
- For 100 cm^3 of solution **K**: 44.4 cm^3

It should be noted that the coexistence of NaCl or SiO$_2$ has no effect on the precipitation titration.

(b) Using the information above, calculate the mass of NaCl produced in the reaction vessel. [6]

- You should consider finding the amount of SiF$_4$ in solution **H**.

....

....

....

....

....

....

....

....

....

....

....

(c) Use your answer in **(b)** and other information to find x. [3]

....

....

....

....

....

....

....

....

....

....

(d) 77.8% of the CCl_4 used as a starting material was unreacted. Calculate the mass of CF$_3$Cl generated. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 17]