

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

(i) Define the *mole*.

[1]

B1 – 1 mole contains 6.02×10^{23} (or Avogadro's Number of) elementary entities.

Do not accept – atoms, molecules, particles etc.

Accept

1 mole contains the equivalent number of carbon-12 atoms in 12 grams of carbon-12.

(ii) Derive the quantity stated in (a).

[2]

With the ideal gas equation $pV = nRT$,

Molar volume is

$$\frac{V}{n} = \frac{RT}{p} = \frac{8.31 \times 293}{101325} = 0.0240 \text{ m}^3 \text{ mol}^{-1} = 24 \text{ dm}^3 \text{ mol}^{-1}$$

M1 – Usage of $pV = nRT$ with correct substitution of values (usage of other values other than those from the Data Booklet is not accepted)

MA1 – Correct conversion from m^3 to dm^3 .

(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]

A2 – All 3 correct (award 1 pt for 2 correct)

- Volume of gas particles is negligible compared to the volume of the container containing the gas particles.
- Negligible interparticle forces of attraction between particles (reject molecules).
- Collision between gas particles and that of a gas particle and the container is elastic.

(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]

A1 – High temperature with explanation

- Interparticle forces of attraction are overcome at high temperature,
- so it can be considered that there are negligible interparticle forces of attraction between particles

A1 – Low pressure with explanation

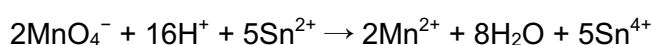
- Relatively low number of molecules

- So volume of gas particles will be negligible compared to volume of container.

Each answer mark is all or nothing.

- (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 $0.0200 \text{ mol dm}^{-3} \text{ KMnO}_4$. 13.50 cm^3 of KMnO_4 was required to reach the end-point. The reaction occurring during the titration is



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

$$n_{\text{Sn}^{2+}} = \frac{5}{2} \times \frac{13.50}{1000} \times 0.0200 = 6.75 \times 10^{-4} \text{ mol}$$

M1 – Finds $n(\text{MnO}_4^-)$

MA1 – Recognising mole ratio of 5/2 and computation of correct answer

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 $0.0200 \text{ mol dm}^{-3} \text{ KMnO}_4$ 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 $\text{Sn}^{2+}/\text{Sn}^{4+}$ ratio in the oxide **F**. [2]

$$n_{\text{Sn}^{2+}}(\text{second titration}) = \frac{5}{2} \times \frac{20.30}{1000} \times 0.0200 = 1.015 \times 10^{-3} \text{ mol}$$

$$n_{\text{Sn}^{4+}} = 1.015 \times 10^{-3} - 6.75 \times 10^{-4} = 3.40 \times 10^{-4} \text{ mol}$$

MA1 – the above. (Allow ECF)

B1 – The ratio is hence 2:1. (Allow ECF only if MA1 mark above is scored.)

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

B1 – Tin(II) oxide: SnO ; Tin(IV) oxide: SnO_2

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

B1 – Sn_3O_4 or $2\text{SnO} \cdot \text{SnO}_2$ (Allow ECF)

- (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]

B1 – Because iron(II) will be further oxidised by MnO_4^- , the second titre value will be higher than expected. (OWTTE)

- Need to show understanding that iron(II) will be oxidised further (at the very least, need to say 'react' if the word 'oxidised' is not present)

- (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 .

G1 – Draws a horizontal line

- 2 density against T , with constant p .

G2 – Draws a $1/x$ graph (inverse proportionality)

Award M1 mark for correct derivation but wrong graph.

Derivation:

$$\begin{aligned} pV &= nRT \\ \frac{m}{V} &= \frac{n}{V} M_r = \frac{p}{RT} M_r \\ \rho &= \frac{p}{RT} M_r = \frac{1}{T} \left(\frac{p}{R} M_r \right) \end{aligned}$$

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

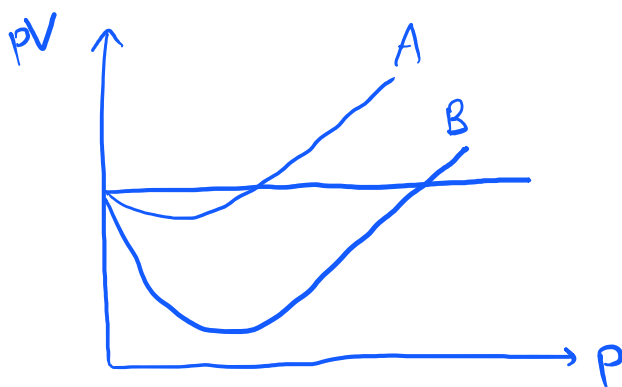
G1 – Draws line passing through origin (line showing direct proportionality)

- (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**.



G1 – Shows deviation for N_2

Accept if candidate draws an upwards sloping straight line, line starts from same vertical intercept.

G1 – Shows greater deviation for NH_3

There are many ways to show this, the idea is to have a much lower turning point and/or more erratic behaviour (e.g. gradient is steeper etc.)

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

[2]

A1 – Explanation for downwards sloping part of graph (Mark is lost when candidate draws only an upwards sloping graph)

- Interparticle forces between gas particles will cause particles to be slightly closer together (compared to an ideal gas), volume of container thus shrinks given a certain pressure

A1 – Explanation for upwards sloping part of graph

- High pressure → Vol. of gas particles are no longer negligible to that of the container → higher V value observed compared to an ideal gas.

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

[1]

A1 – Explains more **significant** intermolecular forces of attraction because...

Hydrogen bonding between NH_3 molecules is more **significant** than dispersion forces between N_2 molecules.

(Reject use of 'stronger')

- 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 $\text{Ce}_2(\text{SO}_4)_3$ ($M_r = 568.424$) dissolved in water (total volume: 200 cm^3)

Titration of 50.0 cm^3 of solution **F** by dropwise adding solution **G** in the presence of xylenol orange 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 $\text{Si}(\text{OH})_4$. 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 $\text{Ce}_2(\text{SO}_4)_3$ reacted in this titration to 4 significant figures. [2]

$$n_{\text{Na}_2\text{SiF}_6} = \frac{0.855}{188.053} \times \frac{50.0}{200} = 0.001137 \text{ mol}$$

$$n_{\text{Ce}_2(\text{SO}_4)_3} = \frac{6.86}{568.424} \times \frac{18.8}{200} = 0.001134 \text{ mol}$$

MA1 each

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

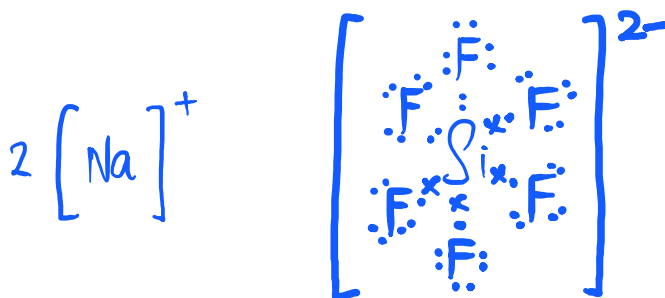
B1 – CeF_3

Hints from preamble

“The generated precipitate is a **binary** compound that contains Ce^{3+} ”

“highly coordinated silicon fluorides also act as **fluorination reagents**”

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



B1 for the above. **There are 2 co-ordinate bonds.**

Si – 4 valence electrons, so there's only 4 Si-F bonds.
 2 other F atoms form co-ordinate bonds with Si. Si is in the 3rd period and can expand octet.

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

From (i), Na_2SiF_6 and $\text{Ce}_2(\text{SO}_4)_3$ reacted in a 1:1 stoichiometric ratio.



Since $\text{Si}(\text{OH})_4$ is formed, the only source of H in a +1 oxidation state is H_2O .

Part 2: Reaction of CCl_4 with Na_2SiF_6

The fluorination reaction of CCl_4 using Na_2SiF_6 was carried out as follows.

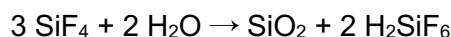
CCl_4 reacts with Na_2SiF_6 to form a chlorofluorocarbon (CFC), of varying number of fluorine atoms in the product (1 to 4). NaCl is the by-product.

x grams of Na_2SiF_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_2SiF_6 and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 dm³ with CCl_4 (solution **H**). Solution **H** only contains SiF_4 as a silicon-containing compound.

A ^{19}F NMR spectrum detects products CFCI_3 , CF_2CI_2 , CF_3CI , 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	CFCI_3	CF_2CI_2	CF_3CI	CF_4
Integration ratio	45.0	65.0	18.0	2.0

SiF_4 is hydrolysed to form H_2SiF_6 according to the following equation.



10.0 cm³ of solution **H** was added to an excess amount of water, which resulted in the complete hydrolysis of SiF_4 . After separation, the H_2SiF_6 generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na_2SiF_6 (aqueous solution **J**).

The precipitate of unreacted Na_2SiF_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 dm³).

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**.

M1 – Demonstrates correct mole ratios

M1 – Finds n_{SiF_4} in 10.0 cm^3 of solution **H**

MA1 – Finds n_{SiF_4} in solution **H** (no ECF)

For 10.0 cm^3 of solution **H**,

$$n_{\text{SiF}_4} = \frac{3}{2} n_{\text{Na}_2\text{SiF}_6} = \frac{3}{2} n_{\text{Ce}_2(\text{SO}_4)_3} = \frac{3}{2} \times \frac{61.6}{200} \times \frac{6.86}{568.424} = 0.005576 \text{ mol}$$

Hence, in 1.00 dm^3 of solution **H**,

$$n_{\text{SiF}_4} = 0.005576 \times \frac{1000}{10.0} = 0.5576 \text{ mol} = 0.558 \text{ mol}$$

M1 – explains why $n_{\text{NaCl}} = 2n_{\text{SiF}_4}$ (best way is to use a balanced chemical equation)

M1 – Calculates n_{NaCl} (allow ECF)

A1 – Correct answer (allow ECF)

Because the only byproduct from the fluorination reaction between Na_2SiF_6 and CCl_4 is SiF_4 , we can construct an equation for this process.



then



and so on...

Hence,

$$n_{\text{NaCl}} = 2n_{\text{SiF}_4} = 2 \times 0.5576 = 1.115 \text{ mol}$$

and

$$\text{mass of NaCl} = 1.115 \times (23.0 + 35.5) = 65.2 \text{ g}$$

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

M1 – Finds amount of unreacted Na_2SiF_6

In 100 cm^3 of solution K,

$$n_{\text{Na}_2\text{SiF}_6} = n_{\text{Ce}_2(\text{SO}_4)_3} = \frac{44.4}{200} \times \frac{6.86}{568.424} = 0.002679\text{ mol}$$

In 10.0 dm^3 of solution K,

$$n_{\text{Na}_2\text{SiF}_6} = 0.002679 \times \frac{10000}{100} = 0.2679\text{ mol}$$

M1 – Finds amount of reacted Na_2SiF_6 (allow ECF since working was from (b))

$$n_{\text{Na}_2\text{SiF}_6} = n_{\text{SiF}_4} = 0.5576\text{ mol}$$

A1 – Correct answer (allow ECF)

$$x = (0.5576 + 0.2679) \times 188.053 = 155$$

No units for x.

- (d) 77.8% of the CCl_4 used as a starting material was unreacted. Calculate the mass of CF_3Cl generated.

[3]

M1 – Finds total amount of products ($n_{\text{CF}_4} + n_{\text{CF}_3\text{Cl}} + n_{\text{CF}_2\text{Cl}_2} + n_{\text{CF}_3\text{Cl}}$)

$$n_{\text{CF}_4} + n_{\text{CF}_3\text{Cl}} + n_{\text{CF}_2\text{Cl}_2} + n_{\text{CF}_3\text{Cl}} = (1 - 0.778) \times \frac{500.0}{12.0 + 4 \times 35.5} = 0.72079\text{ mol}$$

M1 – Calculates mole ratio

The integration ratios in the ^{19}F NMR spectrum are proportional to the number of fluorine nuclei.

Since the number of nuclei is proportional to the amount, the mole ratio can be calculated as such.

^{19}F NMR Data	CFCI_3	CF_2Cl_2	CF_3Cl	CF_4
Integration ratio	45.0	65.0	18.0	2.0
Mole ratio	$\frac{45.0}{1} = 45.0$	$\frac{65.0}{2} = 32.5$	$\frac{18.0}{3} = 6.0$	$\frac{2.0}{4} = 0.5$

MA1 – Correct answer with working

$$\begin{aligned} \text{mass of } \text{CF}_3\text{Cl} &= \frac{6.0}{32.5 + 45.0 + 6.0 + 0.5} \times 0.72079 \times (12.0 + 19.0 \times 3 + 35.5) \\ &= 5.38\text{ g} \end{aligned}$$