SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9746/02

Preliminary Examination **26th August 2009**
Paper 2 Structured **1 hr 30min**
MARK SCHEME

CONFIDENTIAL DOCUMENT

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RECOMMENDED FORMAT OF PRINTING
2 PER PAGE

This document consists of **15** printed pages and **1** blank page

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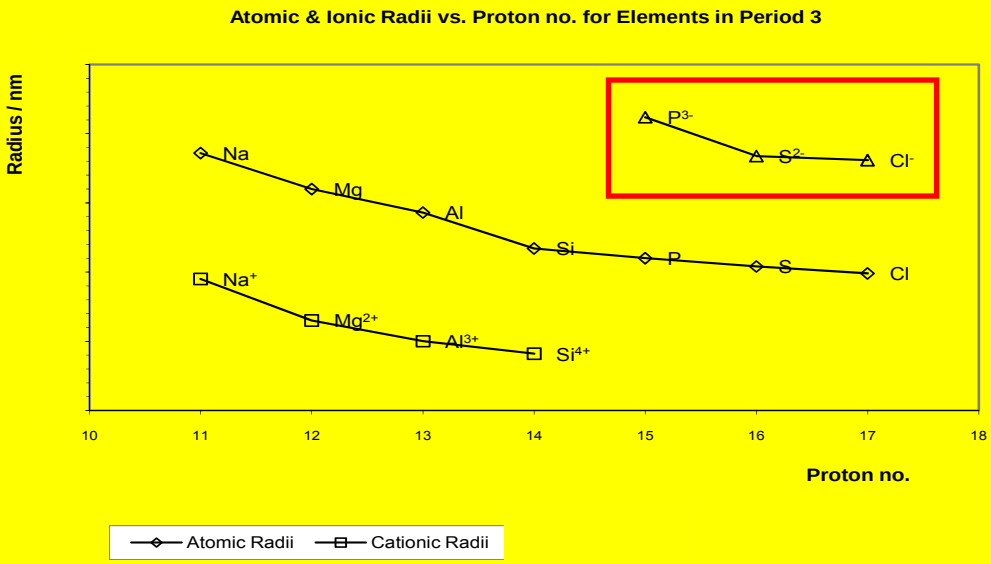
1 The atomic and cationic radii of the Period 3 elements, Na to C*l*, are plotted in the graph below, in order of increasing atomic number.



(a) Explain each of the following:

(i) The atomic radius decreases across the period from Na to C*l*.

Across the period from Na to C*l*,

- **<u>nuclear charge increases</u>** **[1/2M]**;
- but **<u>increase in shielding effect is negligible</u>** as electron is added to the same quantum shell; **[1/2M]**
- Hence, the **<u>effective nuclear charge increases</u>** OR the **<u>electrostatic forces of attraction between the nucleus</u>** and the **<u>outermost/ valence electrons increases</u>** across the period. **[1M]**
- Therefore, the atomic radius decreases across the period from Na to C*l*.

[2]

(ii) The cationic radius of Na^+ is smaller than its atomic radius.

Na^+ has **<u>one electron less</u>** than Na or Na^+ has **<u>one quantum shell less</u>** than Na. **<u>Nuclear charge remains the same</u>**. **[1M]** The **<u>electrostatic forces of attraction between the nucleus and the remaining electrons are greater</u>** for Na^+. **[1M]**

[2]

	(b)	**(i)**	Indicate, on the graph, the relative positions of the ions, P^{3-}, S^{2-} and Cl^-. *Refer to Graph* **[1M]** **[1]**
		(ii)	Explain your answer in **(b)(i)**.
			The anionic radii of P^{3-}, S^{2-} and Cl^- are larger than their respective atoms. This is due to **electrons are being added to the same valence shell**, resulting in **greater inter-electronic repulsions** between the valence electrons. **[1M]** Across the period from P^{3-}, S^{2-} and Cl^-, the anionic radii decrease. The **nuclear charge increases** across the period with **negligible increase in shielding effect** resulting in the corresponding **increase in** the **effective nuclear charge** OR **electrostatic forces of attraction between the nucleus and the valence electrons**. **[1M]** **[2]**
	(c)	**(i)**	Write down the electronic configuration in the ground state for an atom of sulphur.
			$1s^2 2s^2 2p^6 3s^2 3p^4$ or [Ne] $3s^2 3p^4$ **[1M]** **[1]**
		(ii)	Explain the following phenomenon: sulphur can react with fluorine to form SF_2, SF_4 and SF_6 but oxygen can only form OF_2.
			Sulphur is in **Period 3** and hence has the **availability of 3d orbitals** to **expand beyond its octet structure** while oxygen cannot expand its octet due to the absence of d-orbitals. **[1M]** **[1]**
	(d)		The successive ionisation energies in kJ mol^{-1} of an element **A** are as follows: 740, 1500, 7700, 10500, 13600, 18000, 21700 State the Group in which **A** belongs to and explain your answer. Suggest the formula of the chloride of **A**.
			740, 1500, 7700, 10500, 13600, 18000, 21700 760 6200 2800 3100 4400 3700 (difference in IE) - Element A belongs to **Group II** **[1M]** - **Largest energy difference between the 2nd and 3rd IE**. **[1/2M]** - **Removal of the 3rd electron is from an inner quantum shell which requires more energy**. **[1/2M]** Formula: **ACl_2** **[1M]** **[Total: 12]**

2 A pheromone is a chemical substance that, when secreted by an individual of a species, for example the insects, can elicit a certain type of behaviour in other individuals. Compound **B** below is an alarm pheromone secreted by several species of ants, to send out warning signals to other ants.

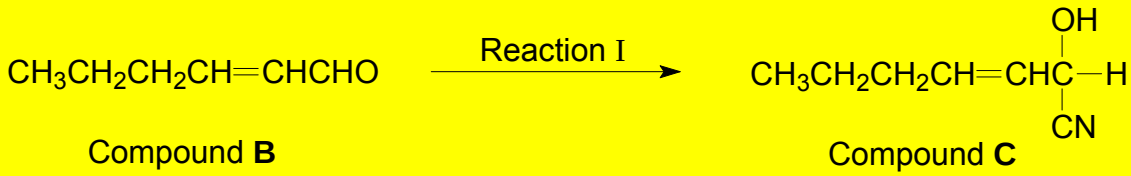
$CH_3CH_2CH_2CH{=}CHCHO$

Compound **B**

(a) Suggest the type of isomerism that exists in compound **B** **[1]**

Geometric Isomerism or **Cis-Trans Isomerism** [1M]

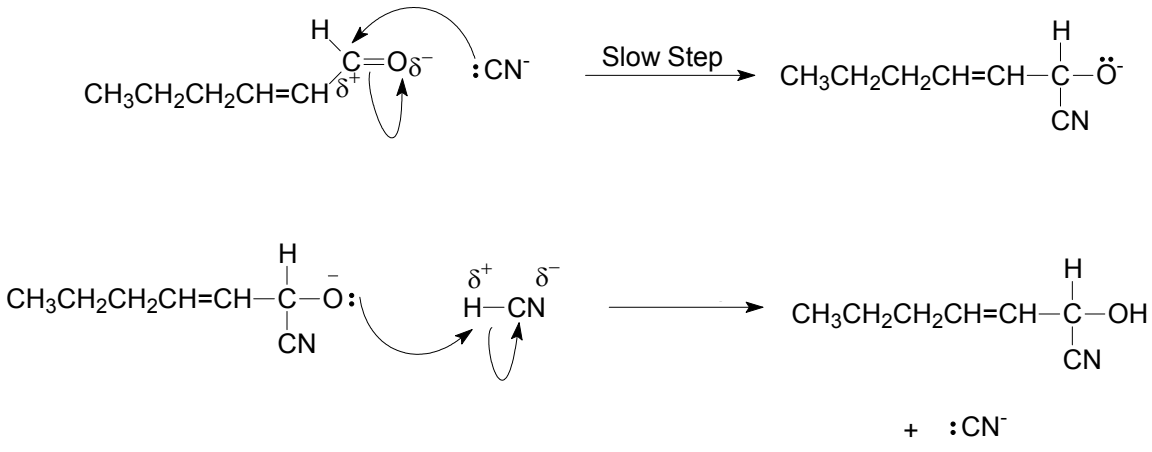
(b) Compound **B** can undergo the following conversion:



Compound **B** Compound **C**

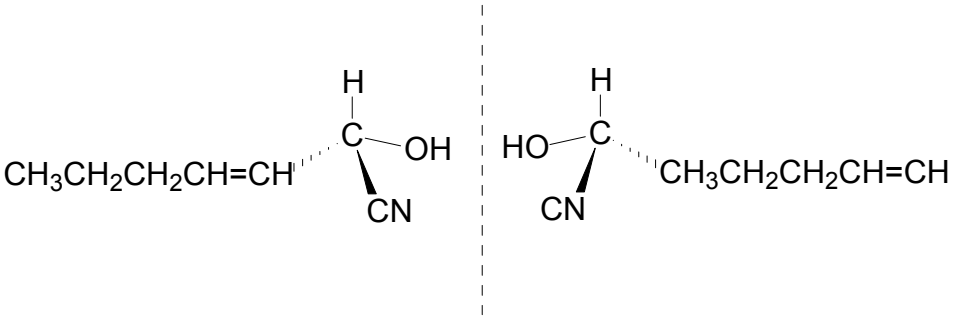
State the reagents and conditions required for the above reaction. Outline the mechanism of the reaction, including curly arrows, showing the movement of electrons, and all charges. **[4]**

Reagents: HCN **[1/2 M]**
Conditions: NaOH (or trace of NaCN), 10-20°C or cold **[1/2 M]**



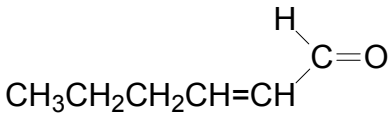
[1M] for curly arrows
[1M] all charges
[1M] for correct intermediate drawn

(c) **(i)** Compound **C** has a chiral carbon. Illustrate the isomerism exhibited with the aid of structural formulae. **[1]**



[1M] **[Comments: invert the molecule]**

(ii) Compound **C**, however, does not rotate plane polarised light. Explain this phenomenon with reference to the mechanism mentioned in **(b)**.

- Carbonyl carbon of compound **B**  is **trigonal planar** **[1/2 M]**
  or
  Carbonyl carbon atom in compound A is **sp^2 hybridised**. Hence, the C atom and the three atoms attached to it lie on the same plane.

- **Nucleophilic attack** on the carbonyl carbon can occur from **either above or below the plane** **[1/2 M]** **and the chance is 50%-50%** **[1/2 M]** **(equally likely)**

- **Racemic mixture is formed** **[1/2 M]** which is optically inactive.
  or
  Both optical forms of compound B will be formed in equimolar which is optically inactive.

(d) The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of nucleophilic substitution reaction:

$$OH^- + CH_3Cl \rightleftharpoons CH_3OH + Cl^-$$

The value of ΔH^θ for the reaction is –75 kJ mol^{-1}, and the value of ΔS^θ is +54 J mol^{-1}.

(i) What is the value of ΔG^θ at 298 K?

$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$
$= (-75 \times 1000) - (298)(54)$
$= -91.1$ kJ mol^{-1} **[1M]**

(ii) Predict whether reaction is feasible at 298 K?

$\Delta G^\theta = -91.1$ kJ $mol^{-1} < 0$, the reaction is feasible. **[1M]**

(iii) Will temperature affect the feasibility of the reaction? Explain.

No. **[1M]**
This is because $\Delta G^o < 0$ at all temperatures. Hence, the reaction is feasible at all temperatures. **[1M]**

[Total: 12]

3 Ammonia is manufactured in the Haber process.

$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) \qquad \Delta H = -92\ kJ\ mol^{-1}$

Le Chatelier's principle predicts that the highest yield of ammonia is obtained at high pressure and low temperature. However, in practice, these conditions are not used.

(a) Using Le Chatelier's principle, explain why the above conditions are used. **[3]**

- At high pressure, the system will try to **reduce the pressure.** **[1/2 M]**
- By Le Chatelier's Principle, position of the **equilibrium** shifts to the **right/forward** **[1/2 M]** towards a **reduction in the number of moles of gas** **[1/2 M]** to decrease the pressure.
- At low temperature, the system will try to **produce more heat** . **[1/2 M]**
- By Le Chatelier's Principle, position of the **equilibrium** shifts to the **right/forward** **[1/2 M]** so as to **produce more heat**, favouring the **exothermic**/**(forward)** **[1/2 M]** reaction .

$\Rightarrow$ yield of ammonia increases.

(b) Suggest two reasons why these particular conditions are not used. **[1]**

Cost/ safety of production **[1/2 M]** using high pressure
Rate of reaction too slow / uneconomical **[1/2 M]** under low temperature.

(c) The gases are usually passed through a tower packed with lumps of metal. Identify the metal used and suggest a reason for the use of this metal. **[2]**

Iron **[1/2 M]** is used as a heterogeneous **catalyst**. **[1/2 M]** as there are **presence of partially filled 3d orbital** which allow the **reactants to be adsorbed onto its surface for reaction** **[1M]** hence increasing the rate of reaction

(d) Under certain conditions, nitrogen and hydrogen are mixed in a 1:3 mole ratio, there is 78% conversion of nitrogen to ammonia at equilibrium. Write an expression for the equilibrium constant K_p. Calculate K_p for this reaction if the total pressure of the equilibrium mixture was found to be 5 x 10^7 Pa. **[3]**

$$K_p = \frac{\left(P_{NH_3}\right)^2}{P_{N_2}\left(P_{H_2}\right)^3}$$ **[1/2 M]**

Let the initial no. of mol of N_2 be x.

	$N_2(g)$ +	$3H_2(g) \rightleftharpoons$	$2NH_3(g)$
Initial no. of mol	x	$3x$	0
Change in no. of mol	$-0.78x$	$-2.34x$	$+1.56x$
No. of mol at Eqm	$0.22x$	$0.66x$	$1.56x$

[1/2 M]

Total no. of mol at equilibrium = $0.22x + 0.66x + 1.56x = 2.44x$ mol

At equilibrium

$$P_{N_2} = \frac{0.22x}{2.44x} \times 5 \times 10^7$$

= 4.501 x 10^6 Pa

$$P_{H_2} = \frac{0.22x}{2.44x} \times 5 \times 10^7$$

= 1.352 x 10^7 Pa

$$P_{NH_3} = \frac{1.56x}{2.44x} \times 5 \times 10^7$$

= 3.197 x 10^7 Pa

[1 M] for correct calculation of all 3 partial pressure

$$K_p = \frac{\left(P_{NH_3}\right)^2}{P_{N_2}\left(P_{H_2}\right)^3}$$

$$= \frac{\left(3.197 \times 10^7\right)^2}{\left(4.501 \times 10^6\right)\left(1.352 \times 10^7\right)^3}$$

= **9.19 x 10^{-14}** **[1/2 M]** **Pa^{-2}** **[1/2 M]**

(e) Calculate the total pressure at equilibrium where ammonia is 90% dissociated into its elements under the same conditions. **[3]**

Let the initial no. of mol of NH_3 be y.

	$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$		
Initial no. of mol	y	0	0
Change in no. of mol	$-0.9y$	$+0.45y$	$+1.35y$
No. of mol at **Eq**^{m}	$0.1y$	$0.45y$	$1.35y$

[1/2 M]

Total no. of mol at equilibrium = $0.1y + 0.45y + 1.35y$
$= 1.90y$ mol

Let P_T be the total pressure at equilibrium.

At equilibrium,

$$P_{N_2} = \frac{0.45y}{1.90y} \times P \qquad P_{H_2} = \frac{1.35y}{1.90y} \times P \qquad P_{NH_3} = \frac{0.1y}{1.90y} \times P$$

[1 M] for correct caln of all 3 partial pressure

$$K_p' = \frac{P_{N_2}\left(P_{H_2}\right)^3}{\left(P_{NH_3}\right)^2}$$

$$\frac{1}{K_p} = \frac{P_{N_2}\left(P_{H_2}\right)^3}{\left(P_{NH_3}\right)^2}$$

$$\frac{1}{9.189\times10^{-14}} = \frac{\left(\frac{0.45}{1.90}P\right)\left(\frac{1.35}{1.90}P\right)^3}{\left(\frac{0.1}{1.90}P\right)^2}$$ **[1 M]**

P_T = **5.96 x 10^5 Pa** **[1/2 M]**

[Total: 12]

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4 A 20.0 cm^3 sample of 0.0100 mol dm^{-3} of ethanoic acid is titrated with 0.0200 mol dm^{-3} of NaOH at 25°C. Given that the K_a of ethanoic acid is 1.80 x 10^{-5} mol dm^{-3},

(a) Explain the term acid dissociation constant, K_a, as applied to ethanoic acid. **[1]**

Acid dissociation constant, K_a is a measure of the **strength of a weak acid**
OR
$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$ **[1M]**

(b) Calculate the initial pH of the 20.0 cm^3 sample of ethanoic acid. **[2]**

$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$
Let the $[H^+]$ be x mol dm^{-3}

$$\frac{(x)(x)}{0.01-x} = K_a$$

Since K_a < 10^{-4} mol dm^{-3}; assume that x is so small that $0.01 - x \approx 0.01$

$$\frac{(x)(x)}{0.01} = 1.8\times10^{-5}$$ **[1 M]**

$[H^+]$ = **4.242 x 10^{-4} mol dm^{-3}** **[1/2 M]**
pH = -lg [4.24 x 10^{-4}]
= **3.37** **[1/2 M]**

(c) Calculate the equivalence volume of NaOH and hence, the end point pH. **[4]**

$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-Na^+(aq) + H_2O(l)$

Amount of CH_3COOH = $\frac{20}{1000}\times0.01$
= 2.000 x 10^{-4} mol

Since $n_{CH3COOH} : n_{NaOH}$ = 1:1

Amount of NaOH = **2.000 x 10^{-4} mol** **[1/2 M]**

Equivalence volume of NaOH = $\frac{2\times10^{-4}}{0.02}$
= **0.0100 dm^3** = **10.0 cm^3** **[1M]**

At equivalence point,

$[CH_3COO^-]$ = $\frac{2\times10^{-4}}{30/1000}$
= 6.667 x 10^{-3} mol dm^{-3} **[1/2 M]**

Let the $[OH^-]$ at equivalence point be y mol dm^{-3}

	$CH_3COO^-(aq)$ +	$H_2O(l)$ ⇌	$CH_3COOH(aq)$ +	$OH^-(aq)$
Initial [ ]:	6.667×10^{-3}	-	0	0
Δ in [ ]:	- y	-	+ y	+ y
Eqm [ ]:	$6.667 \times 10^{-3} - y$	-	y	y

$K_a \times K_b = K_w$

$K_b = \frac{10^{-14}}{1.8 \times 10^{-5}}$

$= 5.556 \times 10^{-10}$ mol dm^{-3} **[1/2 M]**

$$\frac{(y)(y)}{(6.667 \times 10^{3}) - y} = K_b$$

Since $K_b < 10^{-4}$ mol dm^{-3}; assume that *x* is so small that $6.667 \times 10^{-3} - x \approx 6.667 \times 10^{-3}$

$$\frac{(y)(y)}{6.667 \times 10^{3}} = 5.556 \times 10^{-10}$$ **[1/2 M]**

$[OH^-] = 1.924 \times 10^{-6}$ mol dm^{-3}

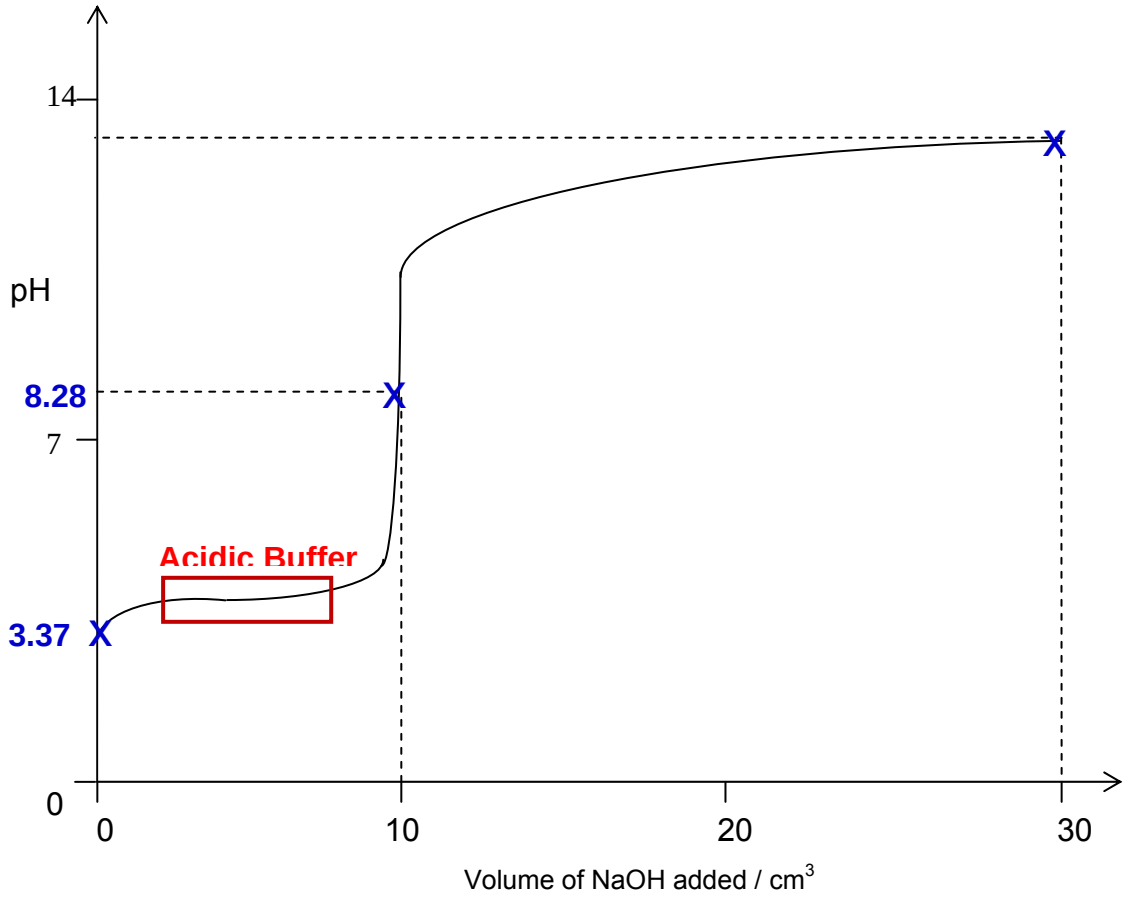
pOH = -lg (1.924×10^{-3}) = 5.716 **[1/2 M]**

pH = 14 – 5.716

= **8.28** **[1/2 M]**

[4]

	(d)	The reaction is continued until 30 cm^3 of sodium hydroxide has been added. On the given grid, using the pH values you have determined from **(b)** and **(c)**, sketch how the pH changes and indicate clearly the buffer region. **[3]**



Mark all 3 points (initial, endpoint and final pH) correctly – **[1M]**
Correct shape of the graph – **[1M]**
Correct indication of buffer region – **1M]**

	(e)	State and explain the choice of a suitable indicator for this reaction. **[2]**

Phenolphthalein. **[1M]**

Its **pH transition range** (≈ 8 – 9.8) **lies within** the sharp **pH change** over the **equivalence point**. **[1M]**

[Total: 12]

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5 (a) A gaseous mixture containing O_3 and N_2O in a 2000 cm^3 gas canister exerts a pressure of 81.06 kPa at 25 °C.

(i) Calculate the total number of moles of gases in the gas canister and hence M_r of the gaseous mixture if the mass of the gaseous mixture is 1.80 g.

$$n = \frac{pV}{RT} = \frac{81.06 \times 10^3 \times 2000 \times 10^{-6}}{8.31 \times (273 + 25)}$$ **[1M]**

= 0.06547

= 0.0655 mol [1M] (to 3 sf)

$$M_r = \frac{1.800}{0.06547}$$ **[1/2 M]** = **27.5 [1/2 M]** **[3]**

(ii) State two assumptions made in your calculations.

The gas particles have **negligible intermolecular forces of attraction[1M]**

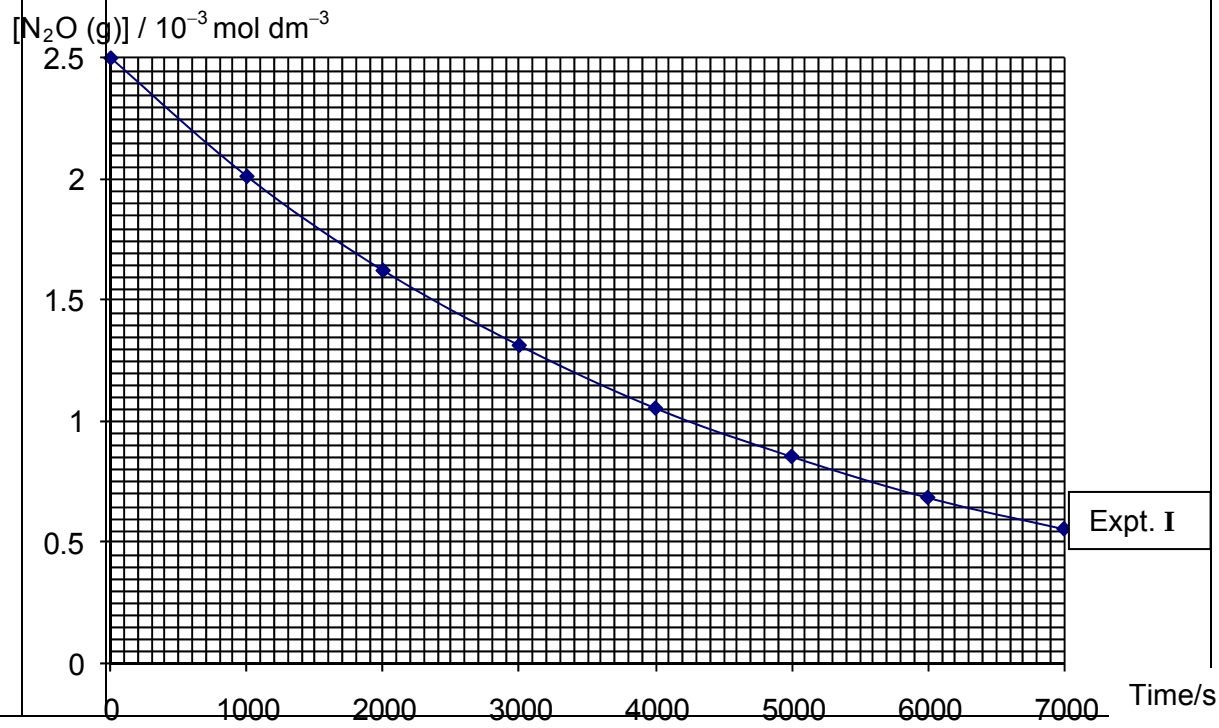
The gas particles have **negligible volume (or size)**. **[1M]**

[2]

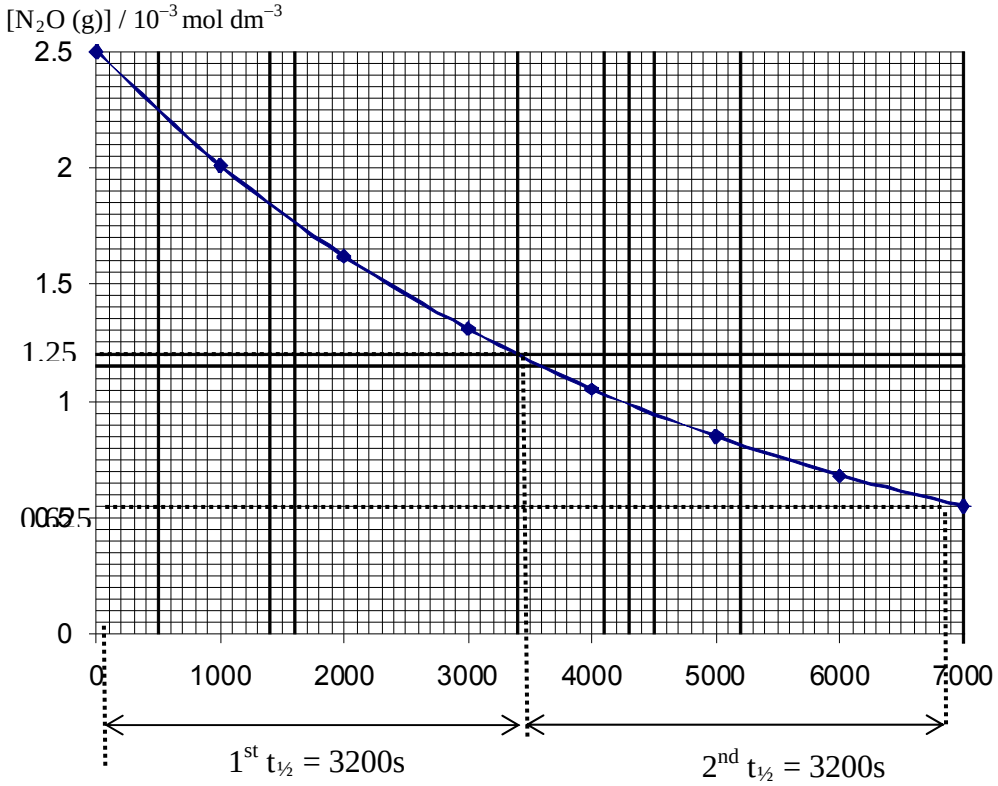
(b) Nitrous oxide or dinitrogen oxide, N_2O, is commonly known as "laughing gas" due to the euphoric effects of inhaling it. It is used in surgery and dentistry for its anaesthetic and analgesic effects. At 1200K, in the presence of gold wire, dinitrogen oxide decomposes as shown:

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g).$$

To follow the rate of reaction, the change in concentration of a sample of N_2O is measured against time. The results are shown below:



(i) Find the order of reaction with respect to N_2O.



Expt. I

Since **half-life = 3200 s** [1M] and is a constant, the order of reaction is **first order** [1M] with respect to N_2O.

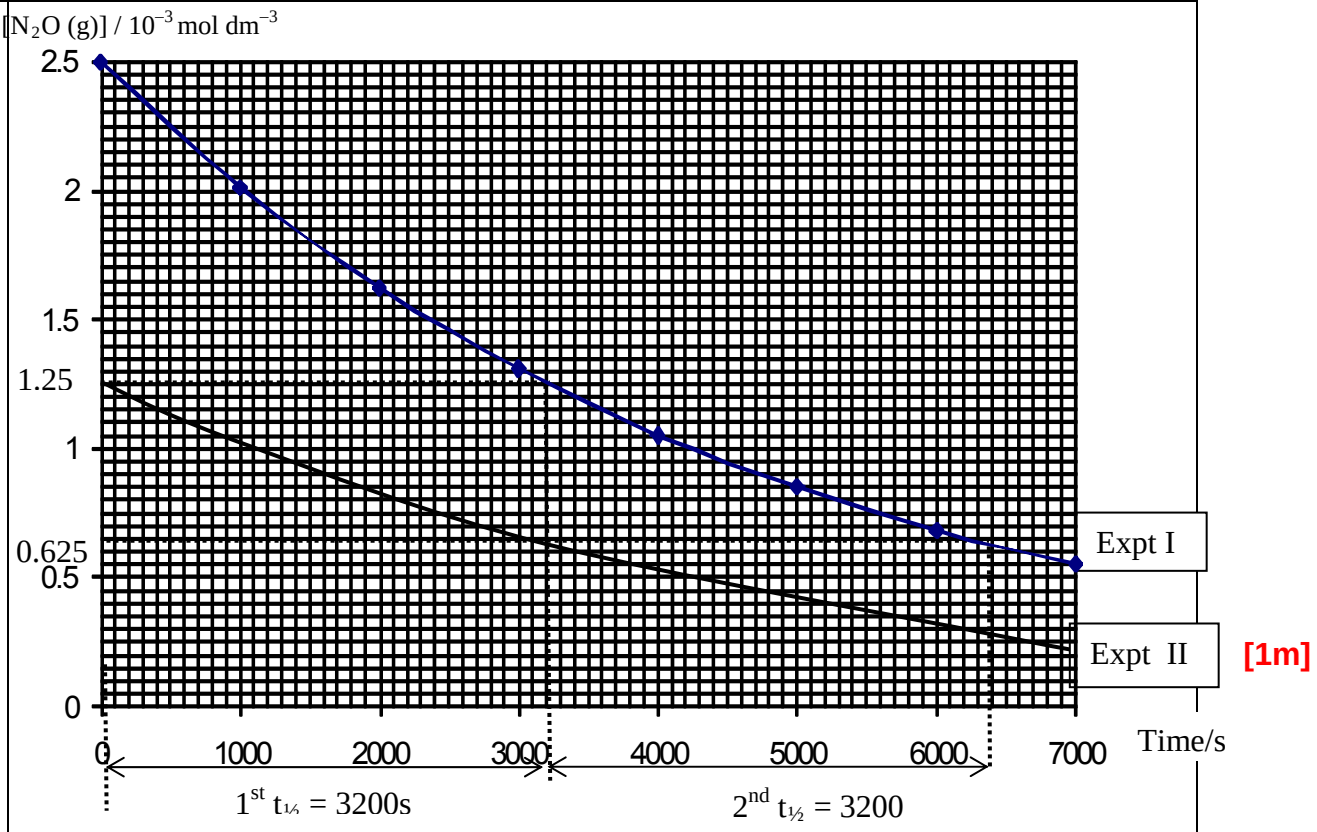
[2]

(ii) Calculate the rate constant for the reaction

Rate constant = $\frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{3200}$ [1/2 M] = **2.17×10^{-4} s^{-1}** [1/2 M]

[1]

(iii) The experiment was repeated using N_2O with an initial concentration of 1.25 x 10^{-3} mol dm^{-3}. On the same axes, sketch the graph of concentration of N_2O against time for this new experiment. Label the graph as Experiment **II**.



[1m]

[1]

(c) Two graphite electrodes were submerged into a beaker containing copper (II) sulphate solution. The circuit was connected to a battery.

(i) State what would be observed at the anode, cathode and the electrolyte after some time.

Anode: bubbles of oxygen gas is seen **[1/2 M]**

Cathode: pink solid of copper metal deposited **[1/2 M]**

Electrolyte: Blue solution decolourised or blue color of the solution becomes lighter.

[1/2 M]

		(ii)	Explain why bubbles of gas are produced at the cathode when the power supply is turned on for a prolonged period of time.
			After a prolonged period of time, **all $Cu^{2+}(aq)$** in the electrolyte at the cathode region has **undergone reaction completely/ reduced to Cu**. **[1/2 M]** **H_2O will undergo reduction to H_2 at the cathode** which explains the gas produced at the cathode. **[1 M]** **[Total: 12]**

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