Name ______________________ Class: 17S_____ Reg Number: _____

MERIDIAN JUNIOR COLLEGE
2017 JC1 Promotional Examination
Higher 2

Chemistry 9729

Section B and C

27 September 2017
2 h 20 min

Additional Materials: Data Booklet
Writing Papers

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number in the spaces at the top of this page.

This booklet contains Section **B** and Section **C**.

Section B: Pg 2 to 19

Answer **all** questions in Section **B** in the spaces provided on the question paper. You are advised to spend about **1 hour 30 minutes** on Section **B**.

Section C: Pg 20 to 24

Answer **all** questions in Section **C** on the foolscap paper. You are advised to spend about **50 minutes** on Section **C**.

Begin each question on a *fresh page* of writing paper.

Hand in Section **C** *separately* from Section **B**.

Fasten your answers for Section **C** using the Cover Page at the back of this booklet.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [ ] at the end of each question or part question.

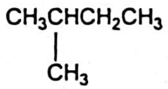
Examiner's Use		
Section A	MCQ	/ 20
Section B	Q1	/ 8
	Q2	/ 9
	Q3	/ 14
	Q4	/ 13
	Q5	/ 16
		/ 60
Section C	Q1	/ 15
	Q2	/ 15
		/ 30
Total		/ 110
Percentage		/ 100
Grade		

This document consists of 24 printed pages and one Cover Page.

Section B: Structured Questions (60 marks)

*You are advised to spend **not** more than **1 h 30 min** on this section.*

1 2–methylbutane is an extremely volatile and flammable liquid at room temperature. It is used in conjunction with liquid nitrogen in cryosectioning in histology.



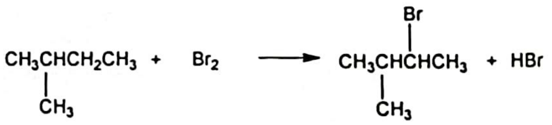
$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$

2–methylbutane

(a) Alkanes are generally unreactive. Suggest a possible reason why this is so. **[1]**

Due to the non–polar nature of alkanes, they are generally unreactive towards polar or ionic reagents like acids, alkalis, or aqueous oxidising agents
OR The C–C and the C–H bond are very strong and requires a large amount of energy to be broken.

(b) 2–methylbutane reacts with bromine gas under ultraviolet light to form a mixture of products. One possible product is 2–bromo–3–methylbutane.



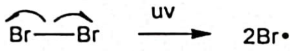
$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_3 + Br_2 \longrightarrow CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{Br}{|}}{C}HCH_3 + HBr$

2–bromo–3–methylbutane

(i) Name and outline the mechanism for the reaction of 2–methylbutane with bromine gas to form 2–bromo–3–methylbutane. **[3]**

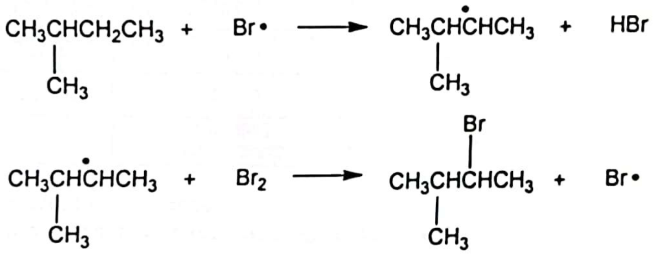
Name of mechanism: Free Radical Substitution

Initiation



$Br—Br \xrightarrow{uv} 2Br\bullet$

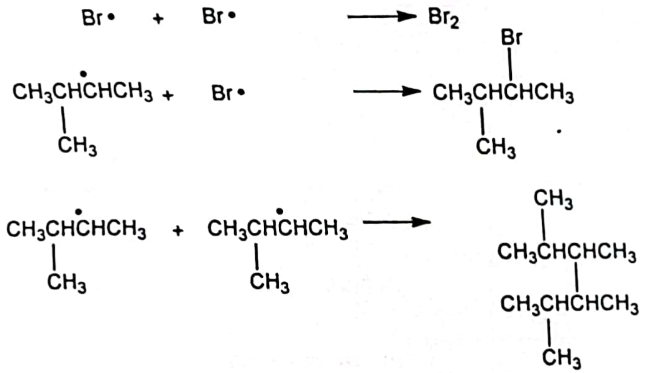
Propagation



$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_3 + Br\bullet \longrightarrow CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\bullet}{C}HCH_3 + HBr$

$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\bullet}{C}HCH_3 + Br_2 \longrightarrow CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{Br}{|}}{C}HCH_3 + Br\bullet$

Termination



$Br\bullet + Br\bullet \rightarrow Br_2$

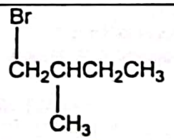
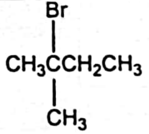
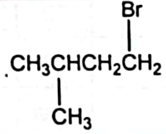
$CH_3CH\dot{C}HCH_3(CH_3) + Br\bullet \rightarrow CH_3CHCBr(H)CH_3(CH_3)$

$CH_3CH\dot{C}HCH_3(CH_3) + CH_3CH\dot{C}HCH_3(CH_3) \rightarrow (CH_3)_2CHCH(CH_3)CH(CH_3)CH(CH_3)_2$

(ii) Other possible isomeric products that could be formed from the reaction of 2–methylbutane and bromine gas are listed in the table below.

Predict the ratio in which these 3 isomeric products are formed.

[1]

	 $BrCH_2CH(CH_3)CH_2CH_3$	 $CH_3CBr(CH_3)CH_2CH_3$	 $CH_3CH(CH_3)CH_2CH_2Br$
Ratio	6	1	3

(c) 2–methylbutane reacts with excess chlorine gas to give a mixture of various chlorinated products such as $C_5H_{11}Cl$, $C_5H_{10}Cl_2$ and $C_5H_9Cl_3$.

In one such reaction, a sample of this mixture of chlorinated products weighing 0.451 g was vaporised at 200 °C and 101 kPa, and found to occupy a volume of 127 cm³.

(i) Calculate the apparent molar mass of the resultant gas mixture.

[2]

$$PV = nRT = \frac{m}{M}RT$$

$$101 \times 10^3 \times 127 \times 10^{-6} = \frac{0.451}{M} \times 8.31 \times (273 + 200)$$

$$M = 138.3 \text{ g mol}^{-1} \text{ (1 d.p.)}$$

(ii) Hence, deduce with reasoning which chlorinated product was present in highest abundance in the mixture.

[1]

	Molar mass / g mol^{-1}
$C_5H_{11}Cl$	106.5
$C_5H_{10}Cl_2$	141.0
$C_5H_9Cl_3$	175.5

Since the apparent molar mass of resultant gas mixture is closest to that of $C_5H_{10}Cl_2$, this means $C_5H_{10}Cl_2$ is in highest abundance in the mixture.

[Total: 8]

2 *This question is related to the atomic properties of gaseous diatomic molecules.*

(a) At low temperatures and pressures, the alkali metals can exist as gaseous diatomic molecules. Recent research has investigated the mixing of gaseous diatomic molecules of different alkali metals (reported in *Science* 2010). Spectroscopic techniques can be used to measure the bond energies of diatomic molecules. When measured in this way, the values of bond energies are given in wavenumbers, which has the unit cm^{-1}.

Some values are shown in the table.

diatomic molecule	Bond energy (BE) / cm^{-1}
K_2	4405
Rb_2	3966
KRb	4180

The enthalpy change, in cm^{-1} for a reaction, ΔH can be determined using the following mathematical expression:

$$\Delta H = \Sigma BE(\text{bonds broken in reactants}) - \Sigma BE(\text{bonds formed in products})$$

(i) Using the expression given above, calculate the enthalpy change, in cm^{-1}, for the reaction between K_2 and Rb_2.

$$K_2(g) + Rb_2(g) \longrightarrow 2KRb(g)$$

[1]

$\Delta H = \Sigma BE(\text{bonds broken in reactants}) - \Sigma BE(\text{bonds formed in products})$

$\Delta H = [BE(K–K) + BE(Rb–Rb)] – [2BE(K–Rb)]$

$\Delta H = [4405 + 3966] - 2[4180]$

$\Delta H = 11.0\ cm^{-1}$

(ii) Complete the electronic configuration of a potassium atom.

[1]

K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(iii) Explain why potassium has a higher first ionisation energy than rubidium.

[2]

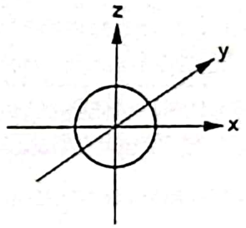
- Atomic radius: Rb > K or size of Rb > K hence valence electrons are further away from the nucleus.
- There is weaker electrostatic attraction between nucleus and the valence electrons of Rb.

(b) Non–metallic diatomic molecules such as halogens Cl_2 and Br_2 are commonly used in halogen incandescent lamps.

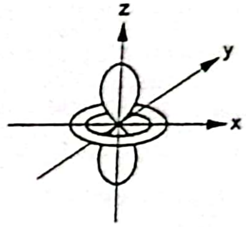
(i) Sketches of the shapes of *some* atomic orbitals from the principal quantum shells of n=3 and n=4 of the bromine atom are shown below in random order.

Suggest a **possible** label for **each** orbital.

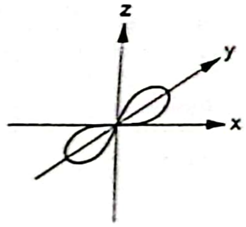
[2]



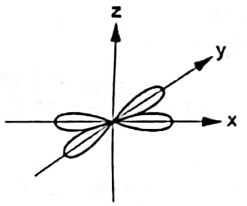
3s or 4s



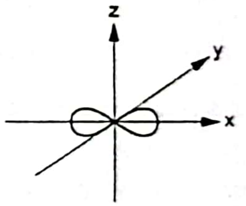
$3d_{z^2}$



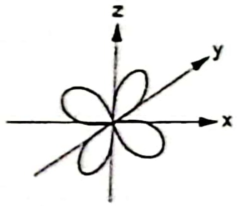
$3p_y$ or $4p_y$



$3d_{(x^2-y^2)}$



$3p_x$ or $4p_x$



$3d_{yz}$

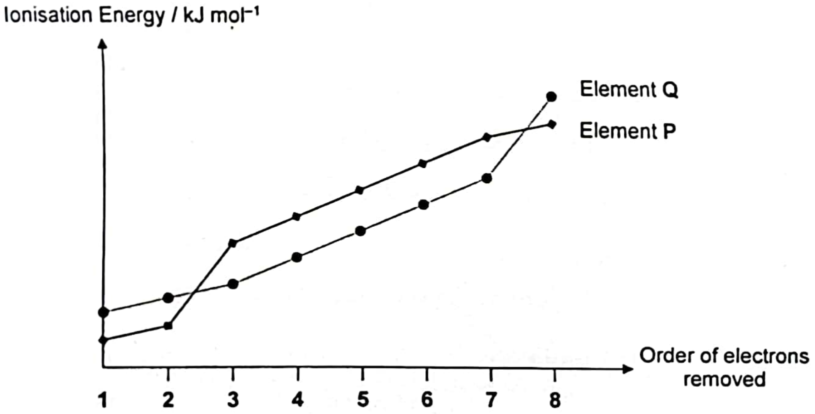
Electronic configuration of Br: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 3d^{10} 4s^2 4p^5$

(ii) The first ionisation energy of bromine is higher than that of selenium. Explain this observation.

[1]

- Nuclear charge of Br > Se but shielding effect is constant; effective nuclear charge of Br > Se
- Strength of electrostatic attraction between nucleus and valence electrons: Br > Se

(c) **P** and **Q** are elements in the third period of the Periodic Table. The figure below shows the ionisation energies when the first eight outermost electrons are removed from each atom of elements **P** and **Q**.



(i) State the Group of the Periodic Table that each element **P** and **Q** belongs to.

[1]

Element **P** belongs to Group 2

Element **Q** belongs to Group 17

(ii) **R** is an element which is in the same Group as element **P**.

R and **Q** can form a corresponding compound that is a non–conductor of electricity in molten state.

Using the above information as well as that from **(c)(i)**, draw the dot–and–cross diagram to illustrate the bonding in the compound formed between **R** and **Q**.

[1]

[Total: 9]

3 Lead(IV) oxide, PbO_2 is an odourless dark–brown crystalline powder. It is sparingly soluble in water and is a strong oxidising agent.

Under basic conditions, solid PbO_2 reacts with solid $Cr(OH)_3$ to form CrO_4^{2-} and PbO_2^{2-} ions.

(a) Write the balanced half–equations and hence construct an overall equation for the reaction between solid PbO_2 and solid $Cr(OH)_3$ under basic conditions.

[2]

Oxidation: $Cr(OH)_3 + 5\,OH^- \longrightarrow CrO_4^{2-} + 4\,H_2O + 3e$

Reduction: $PbO_2 + 2e \longrightarrow PbO_2^{2-}$

Overall: $2\,Cr(OH)_3 + 10\,OH^- + 3\,PbO_2 \longrightarrow 2\,CrO_4^{2-} + 8\,H_2O + 3\,PbO_2^{2-}$

The percentage by mass of PbO_2 in a sample can be determined by the following titrimetric method.

A 5.00 g of sample containing PbO_2 was reacted with excess solid $Cr(OH)_3$ in an alkaline medium. The resultant solution containing CrO_4^{2-} was then diluted to 250 cm^3 in a volumetric flask.

A 25.0 cm^3 aliquot of this diluted solution was then acidified to give $Cr_2O_7^{2-}$ as shown in the following equation:

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

The 25.0 cm^3 aliquot was then titrated against 0.150 mol dm^{-3} aqueous iron(II), Fe^{2+} using a suitable indicator.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The experimental results for the titration are shown in the data table below.

Titration number	**1**	**2**	**3**
Final burette reading / cm^3	25.55	33.75	40.90
Initial burette reading / cm^3	0.00	8.35	15.60
Volume of Fe^{2+} (aq) used / cm^3	25.55	25.40	25.30

(b) Complete the data table above. Using the experimental results, calculate the amount of Fe^{2+} ions required to react with $Cr_2O_7^{2-}$ ions in the 25.0 cm^3 aliquot.

[2]

$$\text{Average volume of } Fe^{2+} \text{ used} = \frac{25.40 + 25.30}{2} = 25.35 \text{ cm}^3$$

$$\text{Amount of } Fe^{2+} \text{ reacted} = 0.150 \times \frac{25.35}{1000} = 3.803 \times 10^{-3} \text{ mol}$$

$$= 3.80 \times 10^{-3} \text{ mol (3 s.f.)}$$

(c) The maximum uncertainty of any single burette reading is ± 0.05 cm³. Calculate the maximum percentage uncertainty in the titre volume calculated in **(b)**.

[1]

$$\% \text{ Uncertainty} = \frac{\pm(0.05+0.05)}{25.35} \times 100\% = \frac{\pm 0.10}{25.35} \times 100\%$$

$$= \pm 0.39\ \% \text{ (2 s.f.)}$$

(d) Calculate the percentage by mass of PbO_2 in the given sample.

[2]

$6Fe^{2+} \equiv Cr_2O_7^{2-} \equiv 2CrO_4^{2-}$

Amount of Fe^{2+} used = 3.803×10^{-3} mol

Amount of $Cr_2O_7^{2-}$ in 25.0 cm³ = $\dfrac{3.803 \times 10^{-3}}{6} = 6.338 \times 10^{-4}$ mol

Amount of CrO_4^{2-} in 25.0 cm³ = $6.338 \times 10^{-4} \times 2 = 1.268 \times 10^{-3}$ mol

Amount of CrO_4^{2-} in 250 cm³ = $1.268 \times 10^{-3} \times \dfrac{250}{25.0} = 0.01268$ mol

$2CrO_4^{2-} \equiv 3PbO_2$

Amount of PbO_2 = $0.01268 \times \dfrac{3}{2} = 0.01901$ mol

Mass of PbO_2 used = 0.01901 x (207.2 + 32.0) = 4.548 g

Percentage by mass of PbO_2 = $\dfrac{4.548}{5.00} \times 100\ \% = 91.0\ \%$ (3 s.f.)

Lead(II) iodide, PbI_2 and lead(II) sulfate, $PbSO_4$ are two commonly used lead–based reagents. PbI_2 exists as a yellow solid while $PbSO_4$ exists as a white solid. Their solubility products, K_{sp} at 20 °C are given in the table below:

Compound	**Numerical value of K_{sp}**
PbI_2	4.4×10^{-9}
$PbSO_4$	2.1×10^{-8}

(e) Suggest using quantitative calculations, which of these two compounds is more soluble in water at 20 °C.

[2]

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

$K_{sp}(PbI_2) = [Pb^{2+}][I^-]^2$
$4.4 \times 10^{-9} = (s)(2s)^2$
$4.4 \times 10^{-9} = 4s^3$

$$s = \sqrt[3]{\frac{4.4 \times 10^{-9}}{4}} = 1.03 \times 10^{-3} \text{ mol dm}^{-3}$$

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp}(PbSO_4) = [Pb^{2+}][SO_4^{2-}]$
$2.1 \times 10^{-8} = (s)(s)$
$2.1 \times 10^{-8} = s^2$

$$s = \sqrt{2.1 \times 10^{-8}} = 1.45 \times 10^{-4} \text{ mol dm}^{-3}$$

PbI_2 is more soluble than $PbSO_4$ because it has a higher solubility.

(f) 50 cm³ of 0.00200 mol dm⁻³ NaI solution and 50 cm³ of 0.00500 mol dm⁻³ Na_2SO_4 solution are mixed at 20 °C. To the resultant solution, 100 cm³ of 0.0100 mol dm⁻³ $Pb(NO_3)_2$ was then added.

State and explain, with the aid of relevant calculations if precipitation will occur. Hence, state the expected observation when these solutions are mixed.

[3]

Ionic product of $PbSO_4 = [Pb^{2+}][SO_4^{2-}]$

$$= \left[\frac{0.0100 \times \frac{100}{1000}}{\frac{200}{1000}}\right]\left[\frac{0.00500 \times \frac{50}{1000}}{\frac{200}{1000}}\right]$$

$= 5.00 \times 10^{-3} \times 1.25 \times 10^{-3}$
$= 6.25 \times 10^{-6}$ mol² dm⁻⁶

Ionic product of $PbSO_4 > K_{sp}(PbSO_4)$

Ionic product of $PbI_2 = [Pb^{2+}][I^-]^2$

$$= \left[\frac{0.0100 \times \frac{100}{1000}}{\frac{200}{1000}}\right]\left[\frac{0.00200 \times \frac{50}{1000}}{\frac{200}{1000}}\right]^2$$

$= 5.00 \times 10^{-3} \times 2.50 \times 10^{-7}$
$= 1.25 \times 10^{-9}$ mol³ dm⁻⁹

Ionic product of $PbI_2 < K_{sp}(PbI_2)$

Hence, only white precipitate of $PbSO_4$ be observed.

(g) State and explain how the solubility of PbI_2 would be affected if PbI_2 is dissolved in an aqueous solution of KI.

[2]

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$ —— (1)

There will be common ion effect due to I^- or identify common ion is I^- By *Le Chatelier's Principle*, equilibrium position in (1) will shift left to decrease $[I^-]$. The solubility of PbI_2 is decreased.

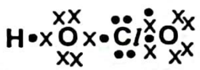
[Total: 14]

4 Chlorous acid, $HClO_2$ is the main component present in '*KlorusKare®*', a disinfectant for food products such as vegetables and seafood.

(a) Chlorous acid contains two central atoms.

(i) Complete the dot-and-cross diagram of chlorous acid, $HClO_2$ in the sketch of the molecule given below.

[1]



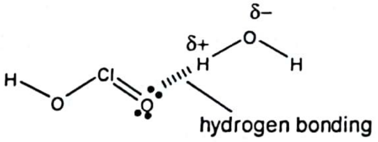
(ii) Using the *Valence Shell Electron Pair Repulsion* theory, state and explain the shape with respect to the chlorine atom.

[2]

- There are 2 bond pairs and 2 lone pairs around central atom or chlorine atom.
- To minimise repulsion, the 4 electron pairs are directed to the corners of a (regular) tetrahedron.
- But lone pair–lone pair repulsion > lone pair–bond pair repulsion > bond pair–bond pair repulsion
- Hence the shape is bent.

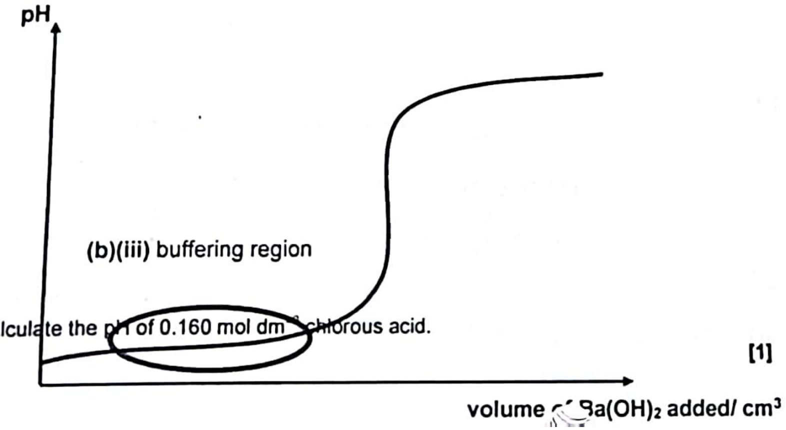
(iii) Draw a labelled diagram to illustrate the solubility of chlorous acid in water.

[1]



Chlorous acid acts as a weak monobasic acid when dissolved in water. The acid dissociation constant, K_a of chlorous acid is 1.10×10^{-2} mol dm^{-3}.

(b) The following sketch of titration curve was obtained when 0.10 mol dm^{-3} $Ba(OH)_2$ was gradually added to a 25.0 cm^3 aqueous solution of 0.160 mol dm^{-3} $HClO_2$ at 25°C.



(i) Calculate the pH of 0.160 mol dm^{-3} chlorous acid.

[1]

$[H^+]$ $= \sqrt{0.16 \times 1.1 \times 10^{-2}}$

$= 4.20 \times 10^{-2}$ mol dm^{-3}

pH $= -\log_{10}(4.20 \times 10^{-2}) = 1.38$

(ii) Determine the equivalence volume of $Ba(OH)_2$ for the titration.

[1]

$$2HClO_2 + Ba(OH)_2 \longrightarrow Ba(ClO_2)_2 + H_2O$$

Initial amount of $HClO_2$ present $= \frac{25.0}{1000} \times 0.160$

$= 4.00 \times 10^{-3}$ mol

$Ba(OH)_2 \equiv 2HClO_2$

Amount of $Ba(OH)_2$ needed $= 2.00 \times 10^{-3}$ mol

Equivalence volume of $Ba(OH)_2 = \frac{2.00 \times 10^{-3}}{0.10} = 0.0200$ dm^3

$= 20.0$ cm^3

(iii) Indicate clearly on the titration curve the region within which the solution is acting as a buffer.

[1]

(iv) Calculate the pH of the resultant solution formed when only 12.0 cm^3 of $Ba(OH)_2$ was added.

[2]

$$2HClO_2 + Ba(OH)_2 \longrightarrow Ba(ClO_2)_2 + H_2O$$

Amount of $Ba(OH)_2$ added $= \frac{12.0}{1000} \times 0.10 = 1.20 \times 10^{-3}$ mol

$Ba(OH)_2 \equiv 2HClO_2 \equiv Ba(ClO_2)_2$

Amount of $HClO_2$ remaining $= 4.00 \times 10^{-3} - 2(1.20 \times 10^{-3}) = 1.60 \times 10^{-3}$ mol

Amount of $Ba(ClO_2)_2$ formed $= 1.20 \times 10^{-3}$ r

Amount of ClO_2^- formed $= 2.40 \times 10^{-3}$ mol

Resulting solution is an acidic buffer containing $HClO_2$ and ClO_2^-

new $[HClO_2] = \frac{0.00160}{0.025 + 0.012} = 0.0432$ mol dm^{-3}

new $[ClO_2^-] = \frac{0.00240}{0.037} = 0.0649$ mol dm^{-3}

$$pH = pK_a + \log_{10}\frac{[ClO_2^-]}{[HClO_2]} = -\log_{10}(1.1 \times 10^{-2}) + \log_{10}\frac{0.0649}{0.0432} = 2.14$$

(v) The pH at the equivalence point of the titration is greater than 7. Suggest an equation to account for the nature of this equivalence point.

[1]

$$\rightleftharpoons$$

$ClO_2^- + H_2O \qquad HClO_2 + OH^-$

The table shows a list of indicators.

Indicator	pH at which colour changes
bromocresol green	3.8 – 5.4
cresol red	7.2 – 8.8
indigo carmine	11.4 – 13.0

(vi) Select the most suitable indicator for the titration, giving a reason for your choice.

[1]

Cresol red. The pH transition range of the indicator lies within the rapid pH change over the equivalence point.

Chloric(I) acid, $HClO$ is an oxidising agent and the chlorate(I) ion, ClO^-, is used as an effective disinfectant in swimming pools.

(c) A solution containing $HClO$ (aq) and $KClO$ (aq) can act as a buffer solution.

With the aid of an equation, explain how the pH of the buffer solution is maintained on addition of small amounts of base.

[2]

$HClO + OH^- \longrightarrow ClO^- + H_2O$

The added OH^- is removed as ClO^- and H_2O.
$[OH^-]$ is slightly changed hence pH *remains* fairly *constant*.

[Total: 13]

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5 This question is about the kinetics of the reaction between peroxydisulfate, $S_2O_8^{2-}$ and iodide.

(a) $S_2O_8^{2-}$ and I^- react in an acidified medium to produce I_2 as follows:

$$S_2O_8^{2-}\,(aq) + 2I^-\,(aq) \longrightarrow 2SO_4^{2-}\,(aq) + I_2\,(aq)$$

The kinetics of this reaction was studied. A fixed volume of starch solution and a small measured volume of $Na_2S_2O_3$ solution were added to an acidified $K_2S_2O_8$ solution. KI solution was then added, and the time taken for the mixture to turn blue–black was measured.

The reaction was repeated using different volumes of KI, with the same volumes of starch, $K_2S_2O_8$ and $Na_2S_2O_3$. Varying amounts of water was also added.

The following results were obtained.

Expt	Volume				Time, t / s	$\frac{1}{t}$ / s^{-1}
	$S_2O_8^{2-}$ / cm^3	I^- / cm^3	H^+ / cm^3	water / cm^3		
1	10.00	20.00	10.00	5.0	15.4	0.0649
2	10.00	15.00	10.00	10.0	20.5	0.0488
3	10.00	10.00	10.00	15.0	30.8	0.0325

(i) Explain why water was added to the reaction mixtures in each of the experiments.

[1]

It is to ensure that total volume is constant so that the volume of reactants is directly proportional to the concentration of reactants in the reaction mixture.

(ii) Deduce the order of reaction with respect to I^- ions.

[2]

Comparing Experiments 1 & 3,
- When $[I^-]$ was doubled, while keeping $[S_2O_8^{2-}]$ and $[H^+]$ constant
- Time taken for blue–black colour appearance is halved (from 30.8 s to 15.4 s)
- Rate of reaction is doubled. Order of reaction w.r.t. I^- is 1

OR

Comparing **Experiments 2 & 3**,
- When $[I^-]$ was increased 1.5 times, while keeping $[S_2O_8^{2-}]$ and $[H^+]$ constant
- Time taken for blue–black colour appearance is decreased 1.5 times (from 30.8 s to 20.5 s)
- Rate of reaction is increased 1.5 times Order of reaction w.r.t. I^- is 1

(iii) Predict what would happen if the reaction was carried out without the addition of $Na_2S_2O_3$ in the reaction mixture.

[1]

Reaction mixture would turn blue–black in colour immediately.

(iv) Suggest a reason why the reaction between $S_2O_8^{2-}$ and I^- ions is unlikely to proceed as an elementary reaction.

[1]

It is very unlikely that the 3 reactants (particles) can collide together with sufficient energy or energy ≥ E_a and with the correct orientation for the reaction to occur.

OR

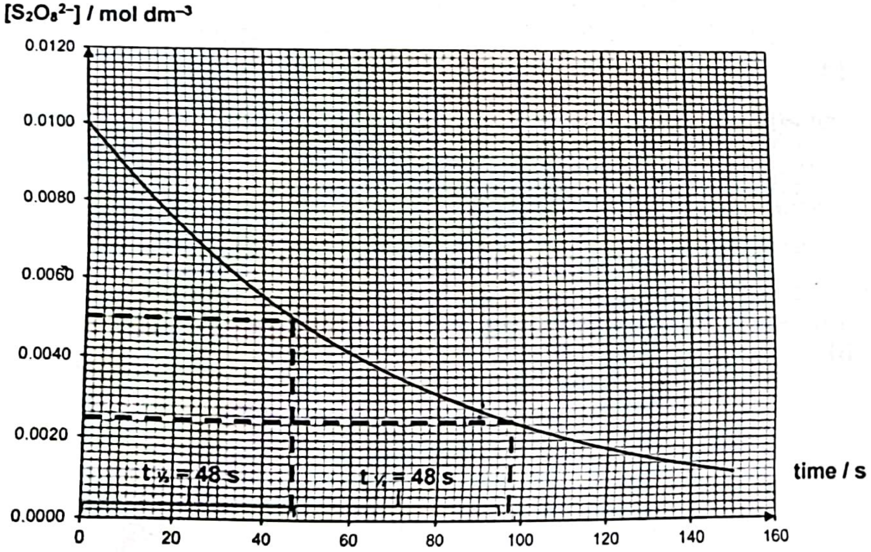
It is very unlikely that the negatively charged reactant particles can collide together with sufficient energy or energy ≥ E_a and with the correct orientation for the reaction to occur.

(b) In another investigation, a 50 cm³ solution of $S_2O_8^{2-}$ was reacted with 50 cm³ solution of acidified I^-, which is in large excess.

10 cm³ portions of the reaction mixture were drawn at various time intervals and transferred into aqueous solution of sodium hydrogen carbonate, $NaHCO_3$ to quench the reaction.

The I_2 produced for each portion was then quantified by titrating the I_2 produced against $Na_2S_2O_3$. The volume of $S_2O_3^{2-}$ required was recorded at various time intervals. The amount of $S_2O_3^{2-}$ used corresponds to the amount of I_2 produced. Correspondingly, the amount of $S_2O_8^{2-}$ that has reacted can be determined.

The progress of the reaction can thus be monitored as a function of concentration of $S_2O_8^{2-}$ remaining against time. The following results were obtained.



(i) Deduce the order of reaction with respect to $S_2O_8^{2-}$ ions. Show your working clearly on the graph.

[2]

From the graph, half–life is <u>constant</u> at <u>48 s.</u> ∴ order of reaction w.r.t. $S_2O_8^{2-}$ = <u>1</u>

((ii) Calculate the rate constant of the reaction between $S_2O_8^{2-}$ and I^-, given that $[I^-]$ is in large excess of 0.500 mol dm⁻³.

[1]

$$t_{½} = \frac{\ln 2}{k[I^-]} = 48\text{ s}$$

$$k = \frac{\ln 2}{t_{½}[I^-]} = \frac{\ln 2}{48 \times 0.500}$$

$$= 0.0289\text{ mol}^{-1}\text{ dm}^{3}\text{ s}^{-1}\text{ (3 s.f.)}$$

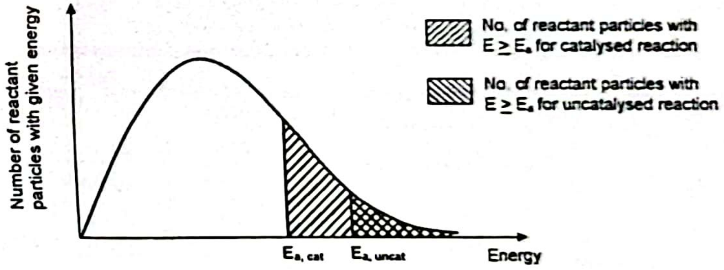
OR

Rate constant determined using actual rate computed from gradient at a point (initial or otherwise), with correct $[S_2O_8^{2-}]$ used. Accept between 0.0260 – 0.0320.

(c) The rate of the reaction between $S_2O_8^{2-}$ and I^- increases when a small amount of a transition metal ion such as Fe^{2+} is added.

(i) With the aid of a Maxwell–Boltzmann distribution curve, explain how the presence of such ions increase the rate of reaction.

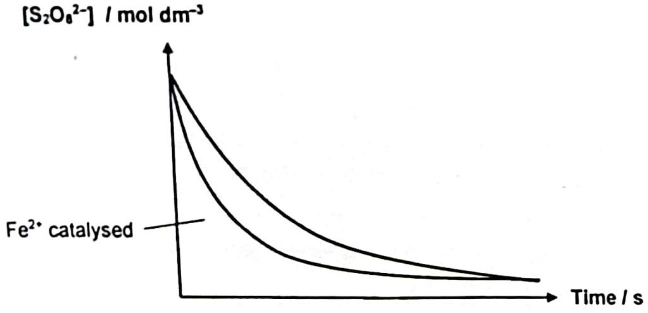
[3]



- The ions acts as a catalyst to increase the rate of reaction by providing an alternative reaction pathway of lower activation energy.
- Number of reactant particles with E ≥ E_a increases.
- Frequency of effective collisions increases.
- Since rate of reaction is proportional to the frequency of effective collisions, rate of reaction increases.

(ii) On the diagram below, sketch the profile of the graph to be expected for the reaction involving Fe^{2+} ions.

[1]



(iii) By means of clear steps, briefly outline the experimental procedure (including any appropriate apparatus) whereby the experiment in **(b)** can be modified to investigate the effect of adding aqueous Fe^{2+}.

[You do **not** need to describe the titration procedure of the quenched iodine portions.]

You may assume that you are provided with the following:

- 0.0100 mol dm^{-3} potassium peroxydisulfate, $K_2S_2O_8$ solution
- 0.500 mol dm^{-3} acidified potassium iodide, KI solution
- 1.00 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$ solution
- 0.100 mol dm^{-3} iron(II) nitrate, $Fe(NO_3)_2$ solution
- stopwatch
- apparatus normally found in a college laboratory

[4]

1. Measure out 50 cm^3 of $K_2S_2O_8$ solution using a **50 cm^3 measuring cylinder**. Transfer into a clean, dry **conical flask**.
2. **Using a 10 cm^3 measuring cylinder**, measure out 5 cm^3 of $Fe(NO_3)_2$ solution into the conical flask containing $K_2S_2O_8$ solution.
3. Using another **10 cm^3 measuring cylinder**, measure out 10 cm^3 of $NaHCO_3$ solution into 6 separate **boiling tubes**.
4. Measure out 50 cm^3 of **acidified KI** solution using a **50 cm^3 measuring cylinder**. Transfer into the conical flask containing the $K_2S_2O_8$ solution and **start** the **stopwatch**.
5. **Using a 10.0 cm^3 pipette, transfer 10 cm^3** of the reaction mixture into a boiling tube containing $NaHCO_3$ at time t = 1 min to stop the reaction.
6. Repeat Step 4 for other time intervals at 3 min, 5 min, 7 min, 9 min.

[Total: 16]

End of Section B

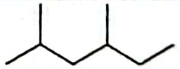
Section C: Free Response Questions (30 marks)

*Answer **ALL** questions in this paper on foolscap paper.*
*Begin each question on a **fresh page** of writing paper.*

*You are advised to spend **not** more than 50 **min** on this section.*

1 Crude oil, commonly known as petroleum, comprises mainly of hydrocarbons. Pentadecane, octane, 2,4–dimethylhexane and benzene are four examples of hydrocarbons that can be obtained from crude oil.

(a) (i) The boiling points of octane and 2,4–dimethylhexane are given below.

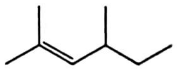
compound	molecular formula	structural formula	boiling point / °C
octane	C_8H_{18}		125
2,4–dimethylhexane	C_8H_{18}		108

Briefly explain why octane has a higher boiling point than 2,4–dimethylhexane.

[2]

- Octane has a straight chain while 2,4–dimethylhexane has a branched chain.
- Extent of surface area of contact : octane > 2,4–dimethylhexane
- Extent of distortion of the electron cloud : octane > 2,4–dimethylhexane
- Extent of intermolecular instantaneous dipole–induced dipole attraction : octane > 2,4–dimethylhexane
- Energy requirement : octane > 2,4–dimethylhexane
- Boiling point: octane > 2,4–dimethylhexane

(ii) 2,4–dimethylhex–2–ene can be reduced to form 2,4–dimethylhexane.

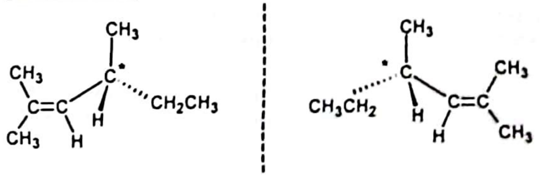


2,4–dimethylhex–2–ene

State the type of isomerism exhibited by 2,4–dimethylhex–2–ene. Draw the structures of the isomers.

[2]

Enantiomerism

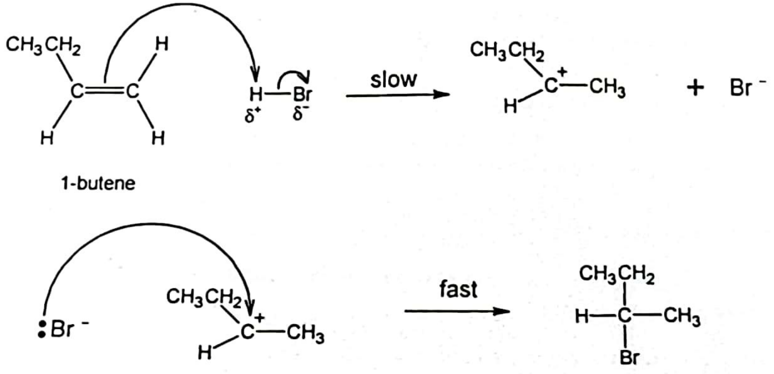


(b) Pentadecane, $C_{15}H_{32}$ can undergo cracking to produce propene, but–1–ene and octane.

(i) Name and outline the mechanism of the reaction between but–1–ene and hydrogen bromide to obtain 2–bromobutane. The mechanism should show curly arrows, charges, dipoles and any relevant lone pairs.

[3]

Name of mechanism: Electrophilic Addition



(ii) Explain why this reaction produces an equimolar mixture of two isomers of 2–bromobutane.

[1]

The Br⁻ / nucleophile can attack the trigonal planar / sp^2 (hybridised C atom of the) carbocation from either the top or bottom of the plane with equal probability.
A racemic mixture is formed containing equal amounts of (+) and (–) enantiomers.

(iii) Describe one simple test–tube reaction you could carry out to distinguish propene from octane.

[2]

Test:
Add bromine dissolved in tetrachloromethane, at r.t.p in the dark to each compound.

Observations:
Propene decolourises reddish–brown bromine solution.
Octane does not decolourises of reddish–brown bromine solution or no colour change is observed

(iv) Suggest the reagents and conditions required in steps **I**, **II** and **III** to carry out the following transformation. Identify the intermediate compound, **X**.

$$CH_3CH{=}CH_2 \xrightarrow{\text{Step I}} X \xrightarrow{\text{Step II}} CH_2{=}CHCH_2Br \xrightarrow{\text{Step III}} CH_2BrCOOH$$

[2]

I: $Br_2(aq)$

II: Excess concentrated H_2SO_4, 170°C or 180°C
OR Al_2O_3 catalyst, 350 °C
OR Excess concentrated H_3PO_4, 250 °C

III: hot acidified $KMnO_4$

X: $CH_3CH(OH)CH_2Br$

(c) Benzene undergoes reduction to form cyclohexa–1,4–diene.

cyclohexa–1,4–diene

Cyclohexa–1,4–diene can also be formed by heating buta–1,3–diene with ethyne.

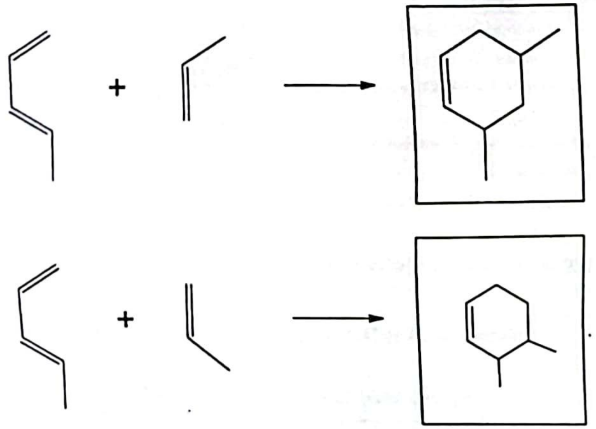
The diagram below shows the movement of electron pairs, represented by curly arrows, needed to generate the cyclohexa–1,4–diene in a single step.

buta–1,3–diene ethyne

In a similar type of reaction, penta–1,3–diene reacts with propene to form two products that are constitutional isomers.

penta-1,3-diene

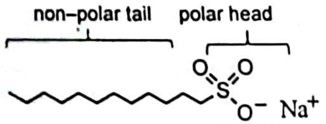
Deduce the structures of these two isomers. **[1]**



(d) Occasionally, seabirds can become contaminated with hydrocarbons from oil spills. The contaminated birds can be cleaned by rubbing vegetable oil into their feathers before their feathers are then lathered with diluted shampoo. The birds are then rinsed thoroughly with water to remove the shampoo and oil.

Photograph of a seabird affected by oil spills
Source: Bird Education Network Bulletin, Issue #32, http://www.birdeducation.org/BENBulletin32.htm
Last accessed 27 Aug 2017

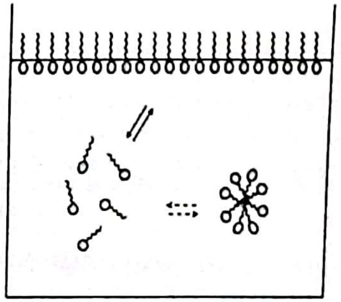
The primary ingredient of a shampoo is a surfactant. A surfactant contains both a discrete polar head and a well–defined non–polar tail. A common surfactant used in shampoos is sodium lauryl sulfate.



sodium lauryl sulfate

simplified representation

When a surfactant is added to water, the molecules orientate themselves on the surface of water as shown in the diagram below. When even more surfactants are added, the surfactant molecules will group together in three–dimensional spherical clusters, with the non–polar tails filling the interior of the cluster and the polar heads composing the outer surface. These molecular clusters are known as *micelles*.



Using your knowledge of chemical bonding and the above information on surfactant and *micelles* formation, comment on the actions taken to treat the affected birds.

- Rubbing vegetable oil into the birds' feathers
- Lathering the feathers with shampoo
- Rinsing the feathers with water

[2]

Hydrocarbon dissolves in vegetable oil since weak instantaneous dipole–induced dipole attractions between hydrocarbon molecules are compatible to the weak instantaneous dipole–induced dipole attractions between vegetable oil molecules.

Mechanical agitation during lathering causes hydrocarbon–oil to be surrounded by surfactant molecules.

The hydrocarbon–oil mixture are broken into small droplets so that relatively small micelles are formed since weak instantaneous dipole–induced dipole attractions between hydrocarbon / oil molecules are compatible to the weak instantaneous dipole–induced dipole attractions between the non–polar tails of the surfactants.

The charged surfaces of the micelles repels each other and prevent the hydrocarbon–oil droplets from coalescing / combining again.

The micelles are easily washed away due the formation of ion–dipole interaction between the polar heads of the micelles and water molecules.

[Total: 15]

2 Sulfur dioxide, SO_2 is a gas with a pungent, irritating smell. While there are many useful applications of sulfur dioxide, SO_2 is also a toxic atmospheric pollutant and is one of the key components in the formation of acid rain.

(a) SO_2 was previously used as a refrigerant as it has a relatively high heat of vapourisation. At 293 K, a 24 dm^3 refrigerant canister containing 1 mol of sulfur dioxide was found to exert an internal pressure of 0.992 atm instead of the theoretically expected 1.00 atm.

Using an assumption of kinetic theory, account for this discrepancy.

[2]

The observed value of 0.992 atm is based on the fact that sulfur dioxide is a real (non–ideal) gas. There are significant (intermolecular) permanent dipole–permanent dipole forces of attractions between molecules. There is less tendency for the molecules to hit the walls of the container *OR* the molecules exert a smaller amount of force on the walls of the container. Hence the observed pressure is smaller than theoretically expected of 1.00 atm.

(b) Sulfur dioxide is an important feedstock in the *Contact Process* to manufacture sulfuric acid industrially. One of the reactions in the *Contact Process* involves the reversible reaction between sulfur dioxide and oxygen.

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \Delta H = -197\ \text{kJ mol}^{-1}$$

In an experiment, a 3:1 ratio of SO_2 and O_2 was mixed at a total initial pressure of 3 atm and was passed over vanadium(V) oxide catalyst at 400 °C in a fixed volume vessel. At equilibrium, the percentage of SO_3 present in the mixture of gases is found to be 60 %.

(i) Write an expression for the equilibrium constant, K_p, for this reaction.

[1]

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})}$$

(ii) Calculate the value of K_p at 400 °C, stating its units, clearly.

[3]

Since total initial pressure = 3 atm, and that SO_2: O_2 is mixed in 3: 1 ratio;
Initial Partial pressure of SO_2 = 2.25 atm
Initial Partial pressure of O_2 = 0.750 atm

	$2\,SO_2(g)$ +	$O_2(g)$ ⇌	$2SO_3(g)$
Initial partial pressure / atm	2.25	0.750	0
Change in partial pressure / atm	$-2x$	$-x$	$+2x$
Equilibrium partial pressure / atm	$2.25 - 2x$	$0.750 - x$	$2x$

Total pressure at equilibrium = $2.25 - 2x + 0.75 - x + 2x = (3 - x)$ atm

% SO_3 present in the mixture of gases = $\dfrac{2x}{3-x} = \dfrac{60}{100} \rightarrow x = 0.6923$ atm

Equilibrium partial pressure of SO_2 = 2.25 – 2 (0.6923) = 0.8654 atm

Equilibrium partial pressure of O_2 = 0.75 – 0.6923 = 0.05769 atm

Equilibrium partial pressure of SO_3 = 2 (0.6923) = 1.385 atm

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})} = \frac{(1.385)^2}{(0.8654)^2(0.05769)}$$

K_p = 44.37 atm = 44.4 atm^{-1}

(iii) How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is increased? Explain your answer.

[2]

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

When pressure in increased, by *Le Chatelier's Principle*, the equilibrium position shifts right to reduce the number of moles of gas, hence decreasing pressure.

The equilibrium mixture contains more products, SO_3 and less reactants, SO_2 and O_2. Thus, the percentage conversion of SO_2 into SO_3 will increase with an increase in pressure.

(iv) Explain why a moderately high temperature of 400 °C was used as one of the operating conditions for this reaction.

[2]

By *Le Chatelier's Principle*, a low temperature will cause the equilibrium position to shift right towards the exothermic reaction to release heat, leading to an increase in yield.

However, too low a temperature would decrease the rate of reaction, making it not feasible industrially.

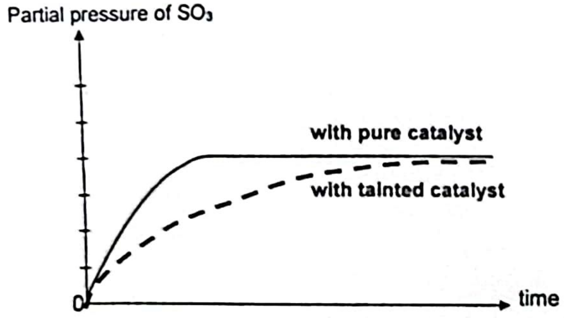
Hence a moderately high temperature of 400 °C is used. Thus, there is a compromise between the conflicting demands of (high) yield and (high) rate of reaction in the conditions. Accept others e.g. balance between yield and high.

(v) In industrial processes such as the *Contact Process*, catalysts are often deactivated in the presence of impurities and loses its efficiency to catalyse the reactions.

The following graph shows how the partial pressure of sulfur trioxide present varies with time at 400°C when pure vanadium(V) oxide catalyst was used.

Transfer the graph below onto the writing paper. Using the same axes, sketch another graph for this experiment to show the variation of partial pressure of SO_3 with time at 400 °C, if the vanadium(V) oxide catalyst was tainted with impurities.

[1]



(c) SO_2 and NO_2 are common atmospheric pollutants that are responsible for the formation of acid rain. While SO_2 can be oxidised atmospherically to form SO_3, there has been no reported formation of NO_3. Suggest an explanation for this observation.

[1]

For N to form NO_3, N would need to have 12 electrons around its valence shell.

N is an element of Period 2, there are no vacant and energetically accessible (d) orbitals for N to expand the octet structure hence NO_3 cannot be formed.

OR

For N to form NO_3, N would need to have an oxidation state of +6. Nitrogen can have a lowest oxidation state of –3 and a highest oxidation state of +5. Hence NO_2 cannot be oxidised to form NO_3.

(d) SO_2 is a reactive chemical species and undergoes different reactions with various compounds.

(i) SO_2 can be removed from exhaust flue gases generated in fossil–fuel power plants by passing the flue gases through a slurry of calcium hydroxide, $Ca(OH)_2$. The reaction between SO_2 and $Ca(OH)_2$ is shown in the following chemical equation.

$$SO_2\,(g) + Ca(OH)_2\,(s) \longrightarrow CaSO_3\,(s) + H_2O\,(l)$$

This reaction can be viewed as an oxide ion transfer from $Ca(OH)_2$ to SO_2. State the role of SO_2 in this reaction.

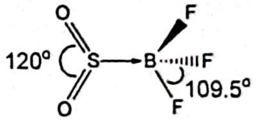
[1]

SO_2 behaves as a Lewis acid OR electron pair acceptor.

$Ca(OH)_2$ behaves as a Lewis base. This reaction involves the Lewis base $Ca(OH)_2$ donating an electron pair (oxide ion, O^{2-}) to the Lewis acid SO_2 to form the sulfite, SO_3^{2-} ion.

(ii) Draw the structure of the adduct formed from the reaction of SO_2 and BF_3, showing clearly the type of bonding, shape and bond angles around the central boron and sulfur atoms.

[2]



[Total: 15]