TEMASEK
JUNIOR COLLEGE

**CHEMISTRY** **9729/03**
Paper 3 Free Response **14th September 2018**
**2 hours**

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

**Section A**
Answer **all** questions.

**Section B**
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

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This document consists of **16** printed pages.

## Section A

Answer **all** the questions in this section.

**1 (a)** There are several stages in the industrial production of methanol from methane.

The first stage involves a gaseous equilibrium between the reactants (methane and steam), and some gaseous products. Figures 1.1 and 1.2 show the percentage conversion of methane into the gaseous products under different conditions at equilibrium.

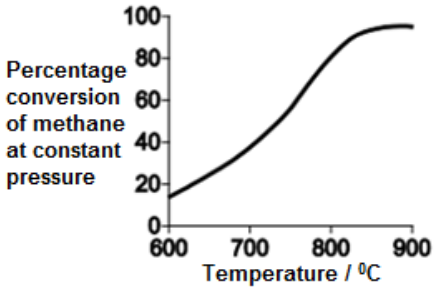



Figure 1.1

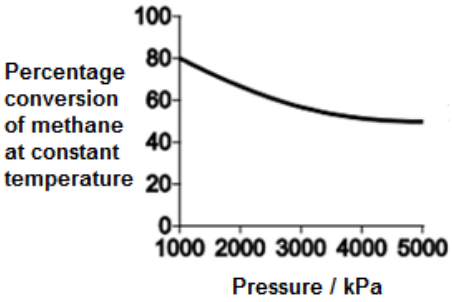



Figure 1.2

**(i)** Use the information from the graphs above to deduce the sign of the

- enthalpy change, $\Delta H$ and
- entropy change, $\Delta S$

for the first stage industrial conversion reaction of methane and steam into the gaseous products. [2]

**• the enthalpy change, $\Delta H$**

**As temperature increases from 600 $^0$C to 880 $^0$C, % conversion of methane increases. This indicates that the forward reaction is favoured as it absorbs energy. Hence, forward reaction is endothermic, $\Delta H$ is positive.**

**• entropy change, $\Delta S$**

**As pressure increases from 1000 kPa to 5000 kPa, % conversion of methane decreases. Forward reaction is not favoured and this indicates that the number of moles of gaseous products particles is more than the gaseous reactants particles. Hence, $\Delta S$ for the forward reaction is positive.**

**(ii)** The optimum temperature for the industrial conversion of methane and steam into the gaseous products is between 780-880$^o$C.

Explain why this is so. [2]

- **Lower than 780 $^0$C, rate of reaction is slow / % conversion is low, hence not cost effective.**
- **Higher than 880 $^0$C, results in high energy costs / expensive & also after a certain temperature, yield does not increase significantly. Therefore, there is no gain in using a higher temperature.**

**(b)** The equation shows the final stage in the production of methanol.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

3.12 moles of carbon monoxide and 5.23 moles of hydrogen were placed in a sealed container. An equilibrium was established at 600 K and the total amount of gaseous molecules was found to be 7.63 moles. The total pressure was 630 kPa.

Calculate the equilibrium constant, $K_p$, for this reaction at 600 K and state its units. [3]

**Let the amount of $CH_3OH$ produced be *x* mol**

| | $CO(g)$ | + | $2H_2(g)$ | $\rightleftharpoons$ | $CH_3OH(g)$ |
|---|---|---|---|---|---|
| Initial/mol | 3.12 | | 5.23 | | - |
| Change/mol | -x | | -2x | | +x |
| Equilibrium/mol | 3.12-x | | 5.23-2x | | x |

**Total moles of gas = (3.12-x) + (5.23-2x) + x = 7.63**

**x = 0.36**

**no. of moles of CO = 2.76; no. of moles of $H_2$ = 4.51; no of moles of $CH_3OH$ = 0.36**

**$P_{(CO)}$ = (2.76/7.63) x 630 = 228 kPa**

**$P_{(H2)}$ = (4.51/7.63) x 630 = 372 kPa**

**$P_{(CH3OH)}$ = (0.36/7.63) x 630 = 29.7 kPa**

$$K_p = \frac{p(CH_3OH)}{p(CO) \times p(H_2)^2}$$

$$K_p = \frac{29.7}{228 \times (372)^2} = 9.41 \times 10^{-7} \text{ kPa}^{-2}$$

- **No. of moles of CO, $H_2$ & $CH_3OH$**
- **Partial pressures of CO; $H_2$ & $CH_3OH$**
- **Correct substitution & value for $K_p$, correct units**

**(c)** Carbon monoxide also reacts with steam.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At 1100 $^0$C, $K_c$ = 1.00

In an experiment, 1 mole of carbon monoxide was mixed with 1 mole of steam, 2 moles of carbon dioxide and 2 moles of hydrogen.

Deduce, with reasons, the direction in which the reaction will shift to reach equilibrium. [2]

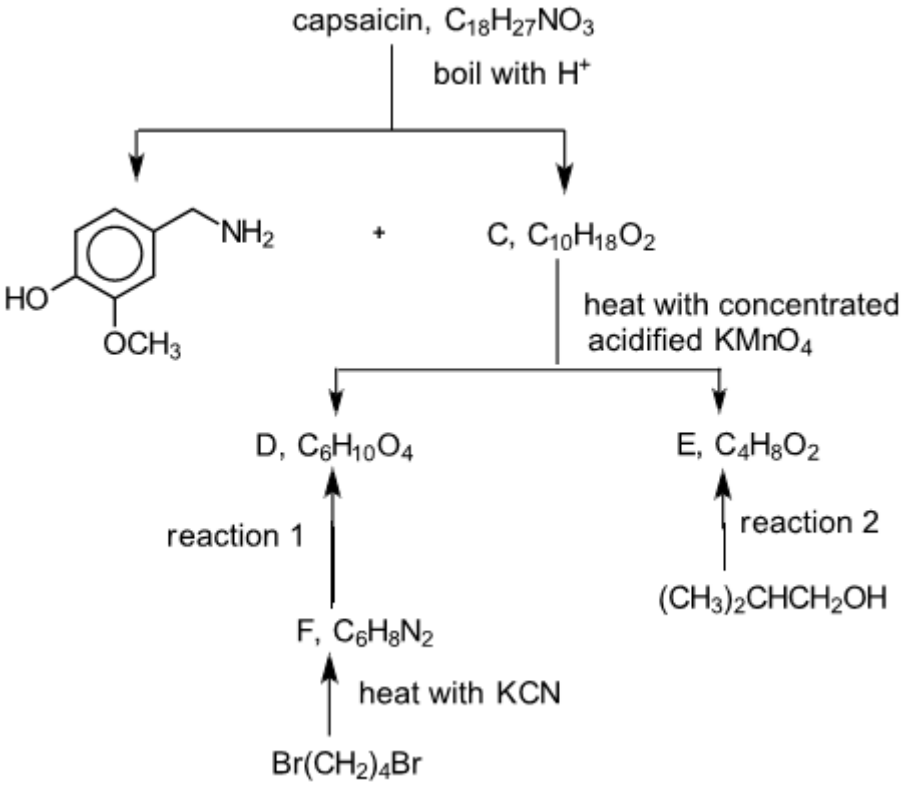
- the quotient / Q:
  $\frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{2 \times 2}{1 \times 1} = 4$, which is larger than $K_c$

**Or $K_c$ = 1, the concentrations of products must be equal to concentrations of the reactants at equilibrium**

**Or Kc = 1, $[CO_2][H_2] = [CO][H_2O]$ at equilibrium**

- **$[CO_2]$ & $[H_2]$ need to decrease and [CO] & $[H_2O]$ need to increase**
  **So position of equilibrium shifts to the left.**

**(d)** The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.



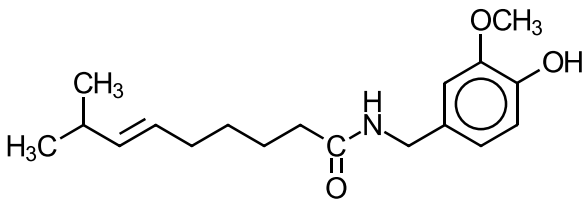

Capsaicin reacts with sodium metal and compounds C, D and E react with $Na_2CO_3(aq)$.

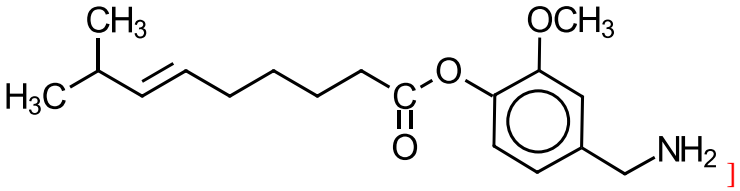
**(i)** Suggest the reagents and conditions for reactions 1 and 2. [2]

- **Reaction 1: Aqueous HCl or $H_2SO_4$, heat**
- **Reaction 2: $KMnO_4$ or $K_2Cr_2O_7$ & dilute $H_2SO_4(aq)$, heat under reflux**

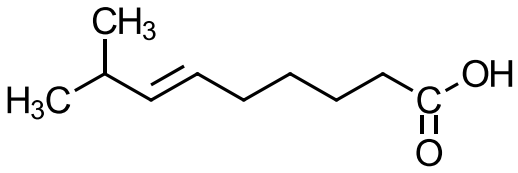
**(ii)** Draw the structural formulae for the compounds C, D, E, F and capsaicin in the above reaction scheme. [5]

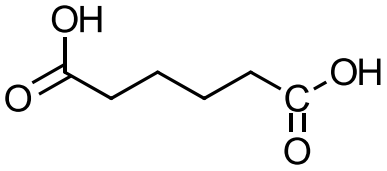
- **Capsaicin:**

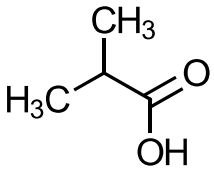


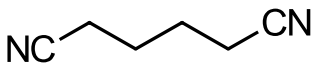




**[Do not accept : ]**

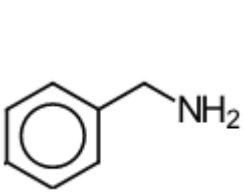
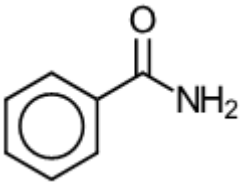
- **C is** 

- **D is** 

- **E is** 

- **F is :** $CN(CH_2)_4CN$ **or** 

**(e)**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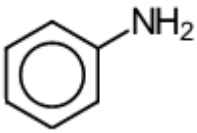


**A** **B** **C**

**A**, **B** and **C** nitrogen containing compounds. State and explain the relative basicities of these 3 compounds. [3]

**Basic strength: B < C < A**

- **A is a stronger base than B & C as the benzyl group,**  **, being electron-releasing in nature, increases the electron density on nitrogen atom. The lone pair of electrons on N is more available for dative bonding to a proton.**

- **The lone pair of electrons on the nitrogen atom of C can be delocalised into the benzene ring, making it less available for dative bonding to a proton. Thus C is a weaker base than A.**

- **B is an amide which is neutral because the lone pair electrons on N is delocalised over O-C-N, i.e:**  **(resonance structure), & hence it is not available for donation to a proton.**

[Total:19]

**2** This question is about nitrogen compounds and their roles in organic synthesis.

Azide is the anion with the formula $N_3^-$. Azide is used as a chemical preservative in hospitals and laboratories.

The azide ion in sodium azide ($NaN_3$) can be oxidised by iodine to form nitrogen gas. To determine the amount of sodium azide in an impure sample, the azide present is first reacted with excess iodine.
The amount of unreacted iodine is then titrated with standard sodium thiosulfate solution:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

0.120 g of an impure sample of sodium azide was dissolved in water. The mixture was reacted with 25.0 $cm^3$ of 0.050 mol $dm^{-3}$ of aqueous iodine. The excess iodine was found to require 23.10 $cm^3$ of 0.040 mol $dm^{-3}$ aqueous sodium thiosulfate for reaction.

**(a) (i)** Write the equation for the azide ion reacting with iodine. [1]

$2N_3^- \rightarrow 3N_2 + 2e$ (x1)

$I_2 + 2e \rightarrow 2I^-$ (x1)

- $2N_3^- + I_2 \rightarrow 3N_2 + 2I^-$

**(ii)** Calculate the percentage purity of sodium azide in the sample. [3]

No. of moles of $Na_2S_2O_3 = \frac{23.10}{1000} \times 0.040 = 9.24 \times 10^{-4}$ mol

- No. of moles of $I_2$ reacted with $Na_2S_2O_3 = \frac{9.24 \times 10^{-4}}{2} = 4.62 \times 10^{-4}$ mol

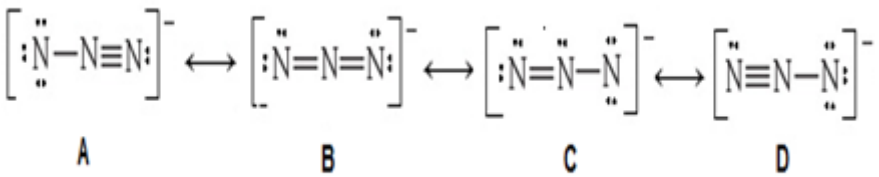
No. of moles of $I_2$ reacted with $NaN_3$

$= \left(\frac{25.0}{1000} \times 0.050\right) - 4.62 \times 10^{-4} = 7.88 \times 10^{-4}$ mol

$2\ NaN_3 \equiv I_2$

- Mass of $NaN_3 = 2 \times 7.88 \times 10^{-4} \times (23 + 14 \times 3) = 0.102$ g
- Percentage purity of $NaN_3 = \frac{0.102}{0.120} \times 100 = 85.4\ \%$

**(b)** A student drew 4 structures **A** to **D** of the linear azide ion in Fig 2.1. His teacher commented one of the structures drawn was incorrect. Determine which is the **incorrect** structure, explaining your answer. [1]



A B C D

Fig. 2.1

- **Structure C is incorrect as it will be bent shape wrt to the central N atom**

**(c)** Azides, being very versatile, can play important roles in organic reactions. An azide ion is called a pseudohalide because it has some properties which are similar to those of chloride ions. As such organic azides, $RN_3$ have similar chemical properties as chloroalkanes.

One organic reaction scheme, involving sodium azide to form amines is shown in Fig 2.2.

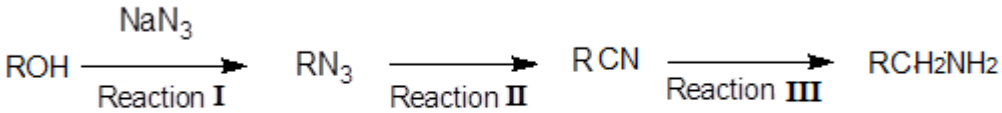


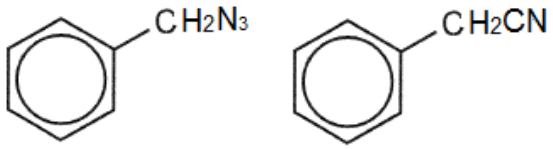

**Fig. 2.2**

**(i)** Identify the role of azide ion in Reaction **I**. [1]

**Nucleophile**

The 3-stage synthesis of compound **E** from compound **B**, makes use of the reaction scheme shown in Fig. 2.2.


**(ii)** Suggest structures for intermediates **C** and **D**, and reagents and conditions for reactions **II** and **III**. [3]




- **C** **D**
- **Reaction II: ethanolic KCN, heat**
- **Reaction III: LiA/H4, dry ether as solvent, room temperature.**

**(iii)** State the *type of reaction* that occur during reaction **III**. [1]

- **Reduction**

A reaction scheme involving compound **B** is shown in Fig.2.3.

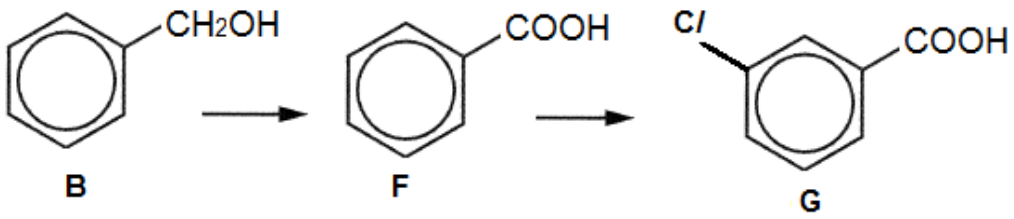



**Fig. 2.3**

**(iv)** Suggest the reagents and conditions for the conversion of **B** to **F** and for **F** to **G**. [2]

- **B to F: acidified $KMnO_4$, heat**
- **F to G: $Cl_2$ gas, anhydrous $AlCl_3$ catalyst, room temperature**

**(v)** Describe and explain how the acidity of **G** would compare to that of **F**. [2]

- **G is a stronger acid than F.**
- **Cl being an electronegative atom helps to disperse the negative charge of the anion formed, making it more stable than the anion of F.**

**(d)** Hydrogen azide, $HN_3$ has a boiling point of 37°C and ammonia, $NH_3$ has a boiling point of -33°C.

**(i)** Suggest a reason for the higher boiling point of hydrogen azide compared to ammonia. [1]

**Both compounds have simple molecular structure and hydrogen bonds exist between molecules. However, $HN_3$ has a larger electron cloud than $NH_3$, which is more easily polarized, this leads to stronger and more extensive instantaneous-dipole induced-dipole attractions, more energy is needed to overcome the id-id attractions, hence $HN_3$ has a higher boiling point than $NH_3$.**

**(ii)** Explain why hydrogen azide is highly soluble in water. [1]

**Hydrogen bonds formed between $HN_3$ and water molecules releases sufficient energy to overcome the hydrogen bonds between $HN_3$ molecules and hydrogen bonds between water molecules.**

**(e)** Nitride is a compound of nitrogen where nitrogen has a oxidation state of -3. Nitrides are a large class of compounds with a wide range of properties and applications.

**(i)** State the electronic configuration of the nitride ion, $N^{3-}$. [1]

**$1s^2 2s^2 2p^6$**

**(ii)** When a beam of nitride ions, $N^{3-}$ was passed through an electric field, it deflected 63° towards the positive plate. Under identical conditions, a beam of azide ions, $N_3^-$ was passed through the electric field. Determine the angle of deflection of the azide ion beam. [1]

**Angle of deflection, $\theta \propto q/m$**
**$\theta m/q$ = constant**
**$\theta_{azide} m_{azide}/q_{azide} = \theta_{nitride} m_{nitride}/q_{nitride}$**

$$\frac{\theta_{azide} \times 42}{1} = \frac{63 \times 14}{3}$$

**$\theta_{azide} = 7°$**

[Total: 18]

**3** Oxalic acid is an organic compound with the formula $H_2C_2O_4$. This colourless solid is a dicarboxylic acid. In terms of acid strength, it is about 3,000 times stronger than ethanoic acid. Its conjugate base, known as oxalate ($C_2O_4^{2-}$), is a reducing agent as well as a bidentate ligand for metal cations.

Oxalic acid dissociates in water according to the following equations.

**I** $HOOC\text{-}COOH + H_2O \rightleftharpoons HOOC\text{-}COO^- + H_3O^+$ $\quad K_{a1} = 5.6 \times 10^{-2}$ mol dm$^{-3}$

**II** $HOOC\text{-}COO^- + H_2O \rightleftharpoons {}^-OOC\text{-}COO^- + H_3O^+$ $\quad K_{a2} = 5.4 \times 10^{-5}$ mol dm$^{-3}$

**(a) (i)** Explain why the value of $K_{a1}$ is larger than $K_{a2}$. [1]

**•The first deprotonation of oxalic acid forms a mono-anion which is stabilised by hydrogen bonding, hence dissociation lies much on the right.**

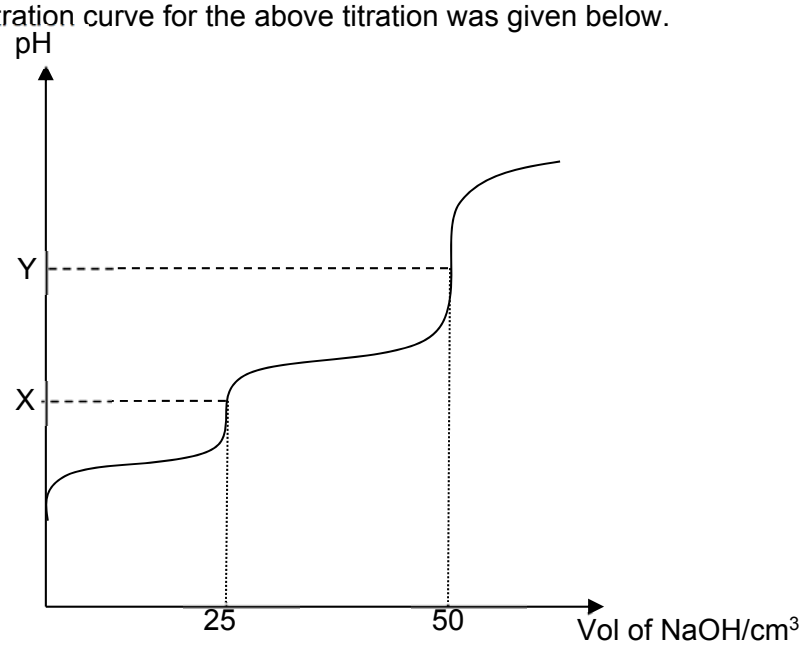
**or HOOC-COOH is a stronger acid than $HOOC\text{-}COO^-$ , as it is more difficult to remove $H^+$ from $HOOC\text{-}COO^-$, a negative ion.**

**(ii)** Write expressions for acid dissociation constants for equation **I** and **II** above. [1]

• **$K_{a1} = \frac{[H_3O^+][HOOC-COO^-]}{[HOOC-COOH]}$** $\quad$ **$K_{a2} = \frac{[H_3O^+][^-OOC-COO^-]}{[HOOC-COO^-]}$**

**(b)** A 25 $cm^3$ sample of oxalic acid of concentration 0.100 mol $dm^{-3}$ was titrated with sodium hydroxide of concentration 0.100 mol $dm^{-3}$.

The titration curve for the above titration was given below.




**(i)** State the major organic species present at points **X** and **Y.** In your answer, include the equation for the reaction that occurred to produce **each** of these two species. [2]

**• Major organic species are $HO_2C–CO_2^-$ and $^-O_2C–CO_2^-$ respectively. The two equations are shown below.**

**• $HOOC\text{-}COOH + OH^- \rightarrow HOOC\text{-}COO^- + H_2O$ step 1**

**$HOOC\text{-}COO^- + OH^- \rightarrow {}^-OOC\text{-}COO^- + H_2O$ step 2**

**(ii)** It has been proven that the $[H_3O^+]$ at the first equivalent point, **X**, is given by the expression,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

Use the given expression to determine the pH value at point **X**. [1]

**$[H_3O^+] = \sqrt{5.6x10^{-2} \text{ x} 5.4x10^{-5}}$ = 1.74 x $10^{-3}$**

**• pH =2.76**

**(iii)** Calculate the pH value at the second equivalent point, **Y**, given that the $[OH^-]$ can be assumed to be entirely due to the hydrolysis of the organic species at Y. [2]

**$^-OOC\text{-}COO^- + H_2O \rightleftharpoons HOOC\text{-}COO^- + OH^-$**

**• $[^-OOC\text{-}COO^-]$ = 25/1000 x 0.1 ÷(25+50)/1000 = 0.0333 mol $dm^{-3}$**

**$K_{b2}$ =** $\dfrac{[OH^-][HOOC-COO^-]}{[^-OOC-COO^-]}$ = $\dfrac{[OH^-]^2}{[^-OOC-COO^-]}$

$K_{b2} = \frac{K_w}{K_{a2}}$ = $10^{-14} \div 5.4 \times 10^{-5} = 1.85 \times 10^{-10}$

$1.85 \times 10^{-10} = \frac{[OH^-]^2}{0.0333}$

$[OH^-] = 2.48 \times 10^{-6}$ mol dm$^{-3}$ , pOH =5.61

- pH = 8.39

OR $[OH^-] = \sqrt{K_{b2}c}$ where $K_{b2} = \frac{K_w}{K_{a2}}$ = $10^{-14} \div 5.4 \times 10^{-5} = 1.85 \times 10^{-10}$

$[OH^-] = \sqrt{(1.85 \times 10^{-10} \times 0.0333)} = 2.48 \times 10^{-6}$ mol dm$^{-3}$ , pOH =5.61

- pH = 8.39

**(c)** Oxalate ions, $C_2O_4^{2-}$, are toxic to the human body. If sufficient amounts are ingested and released into the bloodstream, the high concentration of oxalate ions would cause the precipitation of calcium oxalate in the urine, which can accumulate into painful kidney stones.
Assuming that the body excretes an average of 250 mg of calcium ions per litre of urine, what is the minimum concentration of oxalate ions needed to precipitate calcium oxalate in the urine?
Numerical value of solubility product of calcium oxalate, $CaC_2O_4$= 2.7 x $10^{-9}$. [2]

- conc of $Ca^{2+}$ in urine = (250 x $10^{-3}$/40.1) / 1 mol dm$^3$ = 6.23 x $10^{-3}$ mol dm$^{-3}$

- Minimum concentration of oxalate = 2.7 x $10^{-9}$ / 6.23 x $10^{-3}$ = 4.33 x $10^{-7}$ mol dm$^{-3}$

**(d)** Oxalate ions, $C_2O_4^{2-}$, is also able to combine chemically with certain metals commonly found in the human body. It is able to bond chemically, behaving as a *bidentate* ligand, to transition elements, such as iron to form a complex ion.

$[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6H_2O$ $\quad K_{stab} = 5.00 \times 10^4$

**(i)** What do you understand by the term *bidentate* ligand. [1]

- Bidentate ligand is a ligand which can form <u>two dative bonds</u> with the central metal atom or ion.

**(ii)** Suggest a reason why the stability constant, $K_{stab}$ of the above is greater than 1. [1]

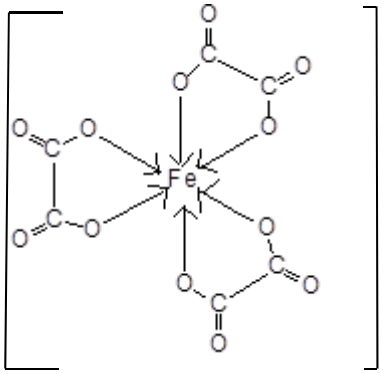
- Bidentate or polydentate ligands, <u>bind more strongly with multiple dative bonds</u> and hence form <u>more stable complexes</u> than $Fe(H_2O)_6^{3+}$.

OR

Complexes involving bidentate or polydentate ligands are more likely to be formed due to an increase in entropy as there is an increase in the number of particles.

**(iii)** Draw the structure of the complex ion, $[Fe(C_2O_4)_3]^{3-}$.Hence suggest the shape for this complex. [2]

•



3-

• **Shape: octahedral**

**(e)** Oxalic acid was one of the products formed when an aromatic organic compound, **A,** with molecular formula $C_{10}H_{10}O_2$ undergoes oxidation with acidified manganate(VII) to form another organic product, **B**, with the molecular formula $C_8H_8O_2$. No other organic compound was formed in the oxidation. Compound **B** reacts readily with 2 moles of $Br_2$(aq) to form compound **E**, $C_8H_6O_2Br_2$. Compounds **A** and **B** are both soluble in NaOH and both **A** and **B** reacts with 2,4-dinitrophenylhydrazine. Compound **A** reacts with acidified dichromate to give an acid, **C**, $C_{10}H_{10}O_3$. Compound **C** reacts with $SOCl_2$ to form a sweet-smelling compound **D**, $C_{10}H_8O_2$.

Suggest structures for **A, B, C, D** and **E** and explain the reactions described. [10]

[Total: 23]

**Explanation:**

**• A, $C_{10}H_{10}O_2$ undergoes oxidation with acidified $KMnO_4$ to form $H_2C_2O_4$ and B, $C_8H_8O_2$. Thus A has a carbon-carbon double bond in the side chain substituent of the benzene ring.**

**• A and B are both soluble in NaOH ⇒ A and B are both acidic forming soluble salts in the acid-base reaction with NaOH. Hence, A and B is either a carboxylic acid or phenol**

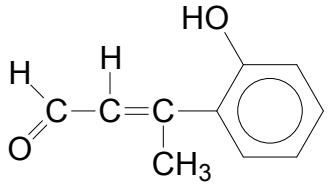
**• B reacts with 2 moles of $Br_2$(aq) ⇒ Electrophilic substitution has taken place and B is a phenol with another substituent either at 2- or 4- position wrt the phenolic group**

**• A and B reacts with 2,4-DNPH ⇒ Condensation reaction has taken place and both A and B contain the carbonyl functional group.**

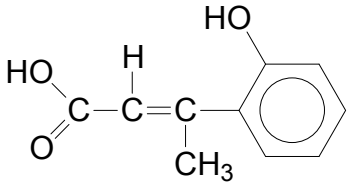
**• A is oxidised by acidified dichromate to form a carboxylic acid, C ⇒ A has an aldehyde group.**

**• C reacts with $SOCl_2$ to form an acid chloride with then reacts with phenol to form a cyclic ester, D. Nucleophilic substitution followed by condensation reaction have taken place.**

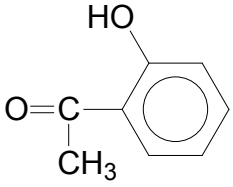
**Compound A:**



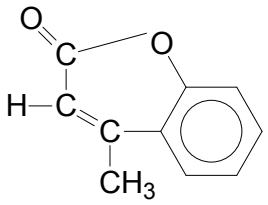
**Compound C:**



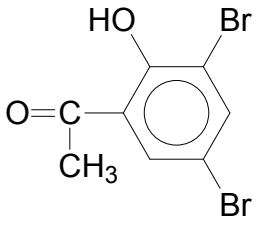
**Compound B:**



**Compound D:**



**Compound E:**



**••••• for structures A, B, C, D and E**

**11 points max 10**

**Turn over for Section B**

**Section B**
Answer **one** question from this section.

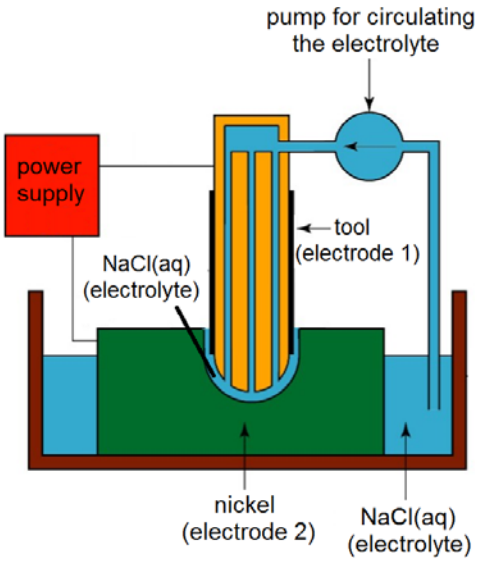
**4** **(a)** Explain, with reference to relevant $E^{\theta}$ values, the industrial process of the electrolytic purification of a copper alloy consisting of nickel and silver impurities. [4]

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^{\ominus} = +0.34\ V$
$Ni^{2+} + 2e^- \rightleftharpoons Ni \quad E^{\ominus} = -0.25\ V$
$Ag^{+} + e^- \rightleftharpoons Ag \quad E^{\ominus} = +0.80\ V$

- **Anode (Oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$**
  **The impure copper is made the anode. Over time, the anode dissolves.**
- **Cathode (Reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ [pure copper]**
  **The electrolyte is made of copper(II) sulfate solution. At the cathode, copper ions are discharged and deposited on the pure copper cathode.**
- **Silver has more positive $E^{\ominus}$ value than $E^{\ominus}_{Cu^{2+}/Cu}$. It will not undergo oxidation at the crude Cu anode and will dislodge from the anode (since there is no substrate support) and fall off as anode mud.**
- **Nickel has less positive $E^{\ominus}$ value than $E^{\ominus}_{Cu^{2+}/Cu}$. Since oxidation occurs at the anode, it will be oxidised together with copper. However, $Ni^{2+}$ will not be reduced at the pure copper cathode as its $E^{\ominus}$ value is less positive than $E^{\ominus}_{Cu^{2+}/Cu}$. Only $Cu^{2+}$ ions will be reduced.**

**(b)** Electrochemical machining is a method used to cut small holes or cavities in metals such as nickel.

The diagram below illustrates the process. The tool (electrode 1) and nickel (electrode 2) are connected to a power supply. The electrodes are in contact with an electrolyte, NaCl(aq), which is being circulated using a pump. Some nickel is then removed by an electrochemical process when the power supply is switched on.




**(i)** State the polarity of each electrode. Write equation for the reaction occurring at each electrode. [2]

- **Electrode 1: Negative (cathode), $2H_2O + 2e \rightarrow H_2 + 2OH^-$**

- **Electrode 2: Positive (anode), $Ni \rightarrow Ni^{2+} + 2e$**

**(ii)** As the process takes place, a green solid is observed in the electrolyte. Suggest the identity of the solid. [1]

- **$Ni(OH)_2$**

**(c)** Magnesium is a Group 2 element that occurs naturally only in combination with other elements. It is the third most abundant element present in seawater, after sodium and chlorine.

**(i)** Describe and explain, using $E^{\ominus}$ values, the relative reactivity of Group 2 elements as reducing agents. [2]

- **Group 2 elements have large negative $E^{\ominus}$ values which become more negative down the Group.**
- **The more negative the $E^{\ominus}$ value, the stronger the reducing power of the element.**

In China, magnesium is produced by electrolysis of molten magnesium chloride. Anhydrous magnesium chloride is fed continuously into electrolytic cells which are hot enough to melt it. Magnesium is produced at the cathode.

**(ii)** Determine the mass of magnesium produced when a current of 40.0 A was passed through one such electrolytic cell for 10 hours. [2]

- **$Q = I \times t = 40 \times 10 \times 60 \times 60 = 1440000$ C**
  **No. of moles of electrons transferred = 1440000 / 96500 = 14.9 mol**
- **Mass of Mg = 14.9 / 2 x 24.3 = 181 g**

The magnesium chloride raw material needed for the electrolysis is obtained from seawater or magnesium chloride-rich brine.

If seawater is used, it is first treated to produce magnesium hydroxide which is then converted to the oxide. The oxide is then heated with carbon in a stream of chlorine at a high temperature as shown in the equation below.

$$2MgO + C + 2Cl_2 \rightarrow 2MgCl_2 + CO_2$$

**(iii)** Identify the oxdising and reducing agents in the above reaction. [1]

**oxidising agent: $Cl_2$**
**reducing agent: C**

On the other hand, if magnesium chloride-rich brine is used, the solution is treated to remove impurities and concentrated by removing water. Dehydration has to be carried out in the presence of hydrogen chloride gas to avoid the reaction of magnesium chloride with water.

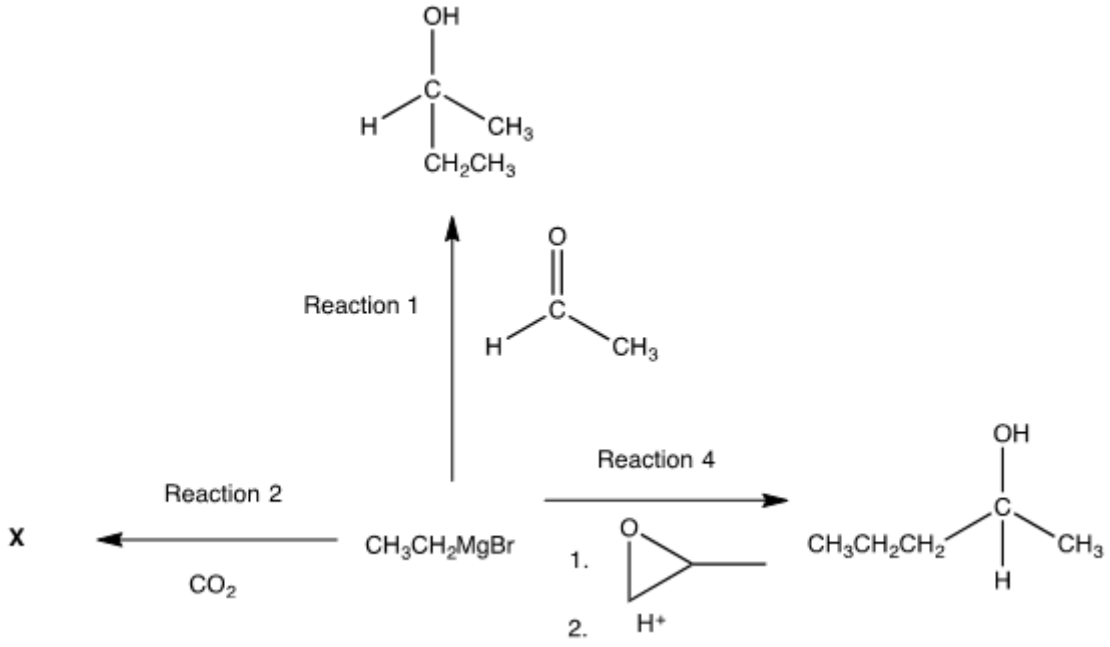
**(iv)** Describe and explain the reaction of magnesium chloride with water. Write equation where appropriate. [2]

- **$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5OH]^{+}(aq) + H^{+}(aq)$**
- **$Mg^{2+}$ has a high charge density hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond. It is easier for a $H^{+}$ ion to leave the water molecule. So the resulting solution is slightly acidic.**

Grignard reagents can be formed from the reaction of magnesium metal with an alkyl or aryl bromide as shown below.

R-Br + Mg → RMgBr  where R represent an alkyl or aryl group

The following reaction scheme shows some reactions involving the Grignard reagent, $CH_3CH_2MgBr$. The Grignard reagent produces the carbanion, $^{-}:CH_2CH_3$, as the reacting species.




**(v)** Suggest the type(s) of reaction that occur in reaction 1 and hence explain why the product mixture obtained is optically inactive. [3]

- **Nucleophilic addition (and protonation/acidic hydrolysis)**
- **$CH_3CH_2MgBr$ can attack the trigonal planar carbonyl carbon either from the top of the plane or the bottom of the plane with equal probability.**
- **This leads to the formation of 2 mirror images which are non-superimposable. Since equal amount of each enantiomer is formed, an optically inactive (racemic) mixture is obtained.**

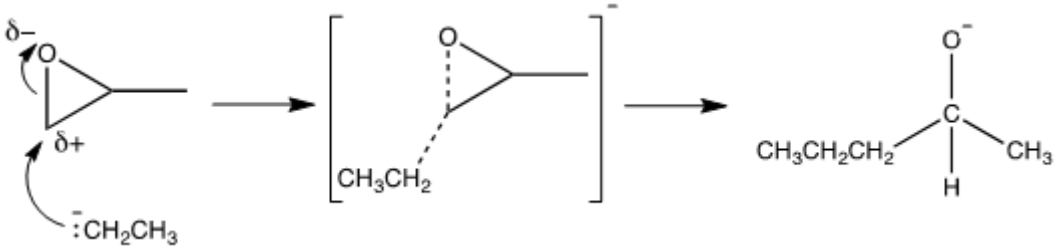
**(vi)** Reaction 2 occurs in a similar manner to reaction 1. Suggest the structural formula of compound **X**. [1]

- **$CH_3CH_2COOH$**

**(vii)** Reaction 3 occurs in two stages.

Stage 1 is a bimolecular nucleophilic substitution reaction.
Stage 2 is a protonation.

Draw the mechanism for stage 1.



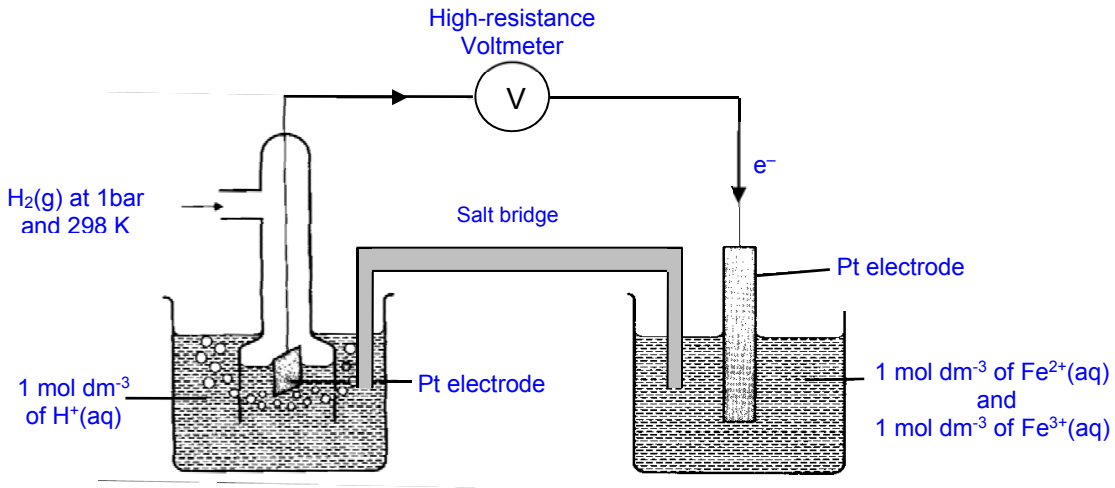

[2]

[Total: 20]

**5** This question is about the chemistry of iron-containing compounds.

**(a)** Iron is the cheapest and one of the most abundant of all metals, comprising nearly 5.6% of the earth's crust and nearly the earth's entire core. It exists in a wide range of oxidation states and undergo redox reactions readily.

**(i)** By means of a fully labelled diagram, describe how the standard electrode potential of the $Fe^{3+}/Fe^{2+}$ system can be measured. Indicate the direction of electron flow. [3]




**[1] – $e^-$ flow [1] – voltmeter, salt bridge + Pt electrodes**

**[1] – $Fe^{3+}/Fe^{2+}$ electrolyte, hydrogen gas inlet & standard conditions**

In Experiment 1, when aqueous iron(III) sulfate is boiled with an excess of potassium cyanide, an orange-red solution is obtained. The solution remains orange-red on addition of aqueous potassium iodide.

In Experiment 2, when aqueous iron(III) sulfate is added to aqueous potassium iodide, a brown solution is obtained.

**(ii)** State the type of reaction that occurred in each experiment. Write a balanced equation for any reaction that occurred. [3]

- **Experiment 1: Ligand substitution**
- **Experiment 2: Redox**
  - **Expt 1: $[Fe(H_2O)_6]^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$**
  - **Expt 2: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$**

**(iii)** With reference to relevant $E^{\ominus}$ values, explain the observation in Experiment 1 upon addition of aqueous potassium iodide. [1]

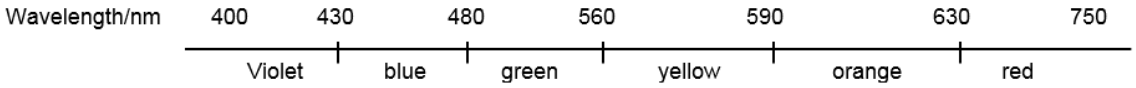
**The orange-red solution is due to the presence of the complex ion $[Fe(CN)_6]^{3-}$.**

- **$E^{\ominus}_{cell} = +0.36 - (+0.54) = \underline{-0.18\ V < 0}$, hence $[Fe(CN)_6]^{3-}$ will not be able to oxidise $I^-$ and the solution remains orange-red.**

**$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$ $E^{\ominus} = +0.36$ V**

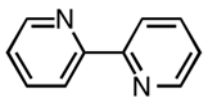
**$I_2 + 2e \rightleftharpoons 2I^-$ $E^{\ominus} = +0.54$ V**

The colour spectrum of the visible region of the electromagnetic spectrum is as shown:




Iron(II) ions form an intense red complex with 2,2'-bipyridine (bipy) according to the following equation:

$$3bipy + Fe^{2+} \rightleftharpoons [Fe(bipy)_3]^{2+}$$



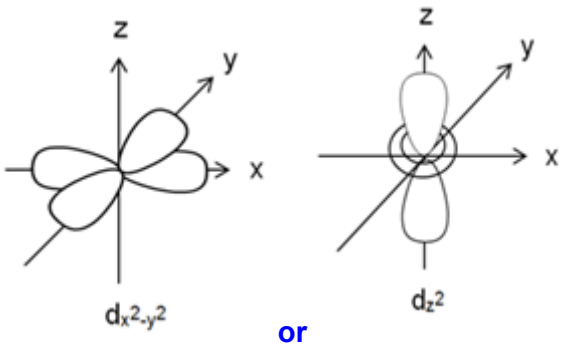

2,2'-bipyridine

The presence of ligands in complexes causes a splitting of the energy of d orbitals into two groups with an energy gap, $\Delta E$, between them.

**(iv)** Given that aqueous iron(II) ion is green in colour, state and explain which ligand, water or 2,2'-bipyridine, results in a larger $\Delta E$. [2]

- **2,2'-bipyridine results in a larger $\Delta E$**
- **$[Fe(bipy)_3]^{2+}$ absorbs green light, which has a <u>higher energy/shorter wavelength</u> than the red light absorbed by $[Fe(H_2O)_6]^{2+}$, which correlates to a larger d orbital splitting.**

**(v)** Draw a labelled diagram of one of the d orbitals at the **higher** energy level in $[Fe(bipy)_3]^{2+}$. [1]




**or**

***Note: The orbitals drawn should be clearly labelled e.g. $d_{x2-y2}$, $d_{z2}$***

**(b)** In the laboratory, iron(II) ions function as a catalyst for the reaction of iodide with hydrogen peroxide.

In an experiment to investigate the kinetics of the reaction, hydrogen peroxide is added to a solution of potassium iodide in the absence of the iron(II) catalyst at 25 °C, and the iodide ions are oxidised according to the equation:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

The following data was obtained.

| Expt | Initial $[I^-]$ / mol $dm^{-3}$ | Initial $[H_2O_2]$ / mol $dm^{-3}$ | Initial $[H^+]$ / mol $dm^{-3}$ | Initial rate of reaction / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|---|
| 1 | 0.01 | 0.01 | 0.0005 | $1.15 \times 10^{-6}$ |
| 2 | 0.01 | 0.02 | 0.0005 | $2.30 \times 10^{-6}$ |
| 3 | 0.02 | 0.01 | 0.0005 | $2.30 \times 10^{-6}$ |
| 4 | 0.01 | 0.01 | 0.001 | $1.15 \times 10^{-6}$ |

**(i)** Use the data above to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction. [3]

**Let the rate equation be: Rate = $k[I^-]^x[H_2O_2]^y[H^+]^z$**

- **From experiments 1 and 4,**
- **When $[I^-]$ and $[H_2O_2]$ are constant and $[H^+]$ is increased by 2 times, initial rate remains unchanged.**
- **Therefore, the order of reaction with respect to $H^+$ is 0.**
- **From experiments 1 and 2,**
- **$1.15 = k\ (0.01)^y$ -------(1)**
- **$2.30 = k\ (0.02)^y$ --------(2) On solving, y = 1**
- **Therefore, the order of reaction with respect to $H_2O_2$ is 1.**
- **From experiments 1 and 3,**
- **$1.15 = k\ (0.01)^y$ -------(1)**
- **$2.30 = k\ (0.02)^y$ --------(2) On solving, x = 1**
- **Therefore, the order of reaction with respect to $I^-$ is 1.**

**Working (2m):**
3 points – 2m
2 points – 1m
1 point – 0m

**Rate eqn (1m)**

- **Rate = $k[I^-][H_2O_2]$**

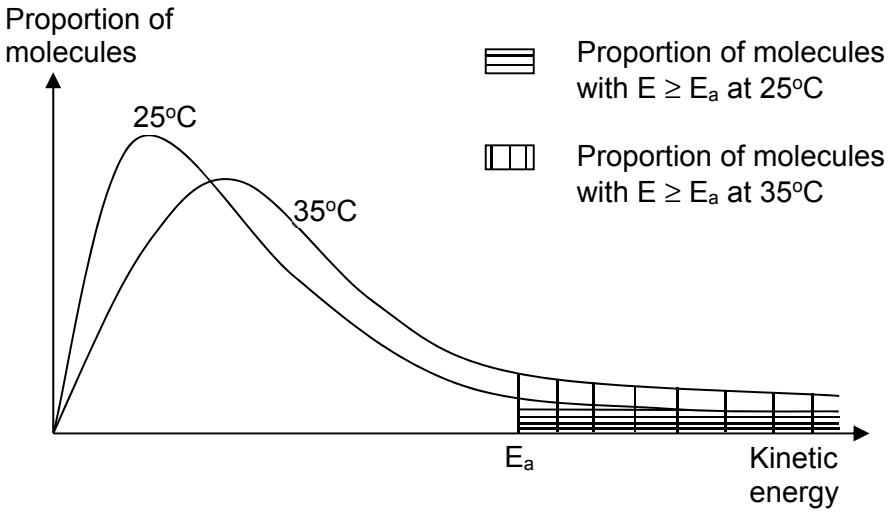
**(ii)** Calculate a value for the rate constant. Include units in your answer. [1]

**Rate = $k[I^-][H_2O_2]$**

**Using Expt 1 data,**

**Rate constant, k = $\frac{1.15\times10^{-6}}{(0.01)(0.01)}$ = 0.0115 $mol^{-1}dm^3s^{-1}$ (units must be correct)**

**(iii)** Explain, with the aid of a suitable diagram, why the rate of decomposition of hydrogen peroxide is expected to proceed faster at 35 °C. [2]




- **well labelled diagram**

- **At higher temperature, average kinetic energy of molecules increases and the proportion of molecules with $E \geq E_a$ increases.**

  **Hence frequency of effective collisions increases and rate of reaction increases.**

**(c)** Some protein-built enzymes form complexes with the metal ions at their active site. An example is catalase, which is an enzyme in the liver that breaks down harmful hydrogen peroxide into oxygen and water. It contains four iron-containing heme groups that allow the enzyme to react with the hydrogen peroxide.

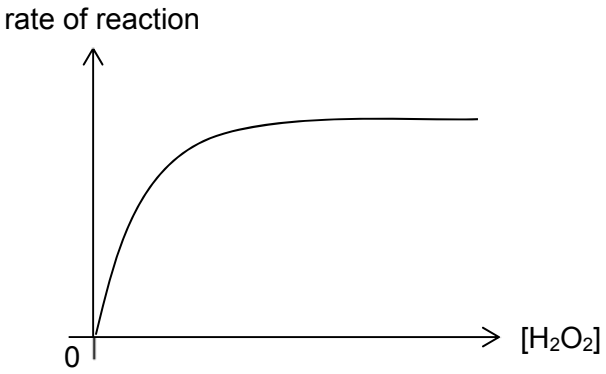
The decomposition of hydrogen peroxide solution to form water and oxygen gas is as shown:

$$2H_2O_2(aq) \xrightarrow{\text{catalase}} 2H_2O(l) + O_2(g)$$

**(i)** What do you understand by the term *enzyme*? [1]

- **Enzymes are highly specific in the type of reaction(s) which they catalyse, which no other enzymes will catalyse.**

**(ii)** A series of experiments were carried out to study the effect of hydrogen peroxide concentration on the rate of reaction, by using different concentrations of hydrogen peroxide at 25 °C. The following graph was obtained.




Account for the shape of the graph. [3]

- **At low $[H_2O_2]$, rate of reaction is directly proportional to $[H_2O_2]$ since active sites are not fully occupied. Hence reaction is first order.**
- **As $[H_2O_2]$ increases, the rate increases to a lesser extent and is no longer proportional to $[H_2O_2]$ since more active sites are occupied. Hence reaction is mixed order.**
- **With further increase in $[H_2O_2]$, rate becomes constant as the enzyme is saturated. Hence reaction is zero order.**

[Total: 20]