



**Catholic Junior College**  
**JC2 Preliminary Examinations**  
**Higher 2**

**CANDIDATE  
NAME**

**CLASS**

**2T**

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**CHEMISTRY**

**9729/03**

Paper 3 Free Response

**Friday 24 August 2018**

**2 hours**

Candidates answer on separate paper.

Additional Materials:      Answer Paper  
                                         Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

**WORKED SOLUTIONS**

### Section A

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

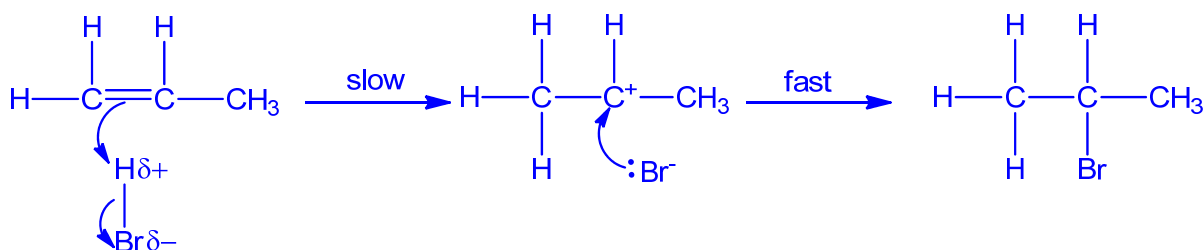
- 1 Propene is a colourless gas that is produced in large quantities by the petrochemical industry. It is used in the production of synthetic rubber and as a propellant in aerosols.

(a) When propene reacts with HBr, 2-bromopropane is produced as the major product.



- (i) Describe the mechanism of the above reaction, using curly arrows to show the movement of electrons. [4]

#### Electrophilic addition

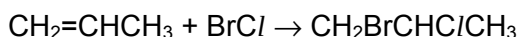


Correct partial charges, lone pair of electrons, slow/fast steps

Correct curly arrows

Correct secondary carbocation intermediate

- (ii) When propene reacts with BrCl, 1-bromo-2-chloropropane is produced as the major product.



With reference to your answer in (i), explain why the two reactions give major products with bromine in different positions. [2]

Br is more electronegative than H but less electronegative than Cl, hence Br acquires a partial positive charge in BrCl. Thus, Br adds first to form the more stable carbocation where the positive charge is on the second carbon

- (iii) The product of the reaction in (ii) has a chiral carbon, but it is optically inactive. Explain why this is so. [2]

There is equal chance of Cl<sup>-</sup> attacking the trigonal planar carbon in the carbocation intermediate from either side of the plane. Thus, both enantiomers are formed in equal amounts/a racemic mixture is formed.

- (b) 2-bromopropene reacts with hot aqueous sodium hydroxide, whereas 2-bromopropane does not. Suggest reasons for this difference in reactivity. [2]

In 2-bromopropene, p orbitals of Br overlap with  $\pi$  bond (one of the lone pairs of electrons on Br is delocalised into the C=C  $\pi$  bond), hence there is a partial double bond character for the C-Br bond. This makes the C-Br bond stronger and harder to break for nucleophilic substitution to occur.

The carbon of the C-Br bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks.

The electron rich C=C  $\pi$  bond will repel the negatively charged incoming nucleophile, hence the attack of the nucleophile will be less likely to occur.

- (c) Propene can undergo mild oxidation in the presence of cold acidified potassium manganate(VII), to give  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_3$ .

- (i) State the IUPAC name of the product of the above reaction. [1]

**Propane-1,2-diol**

- (ii) Construct the half-equation for the oxidation of propene as described above. [1]



- (iii) Hence, write the equation for the overall reaction, showing clearly the stoichiometry of reaction between propene and manganate(VII) ions. [1]



- (d) At room temperature and pressure, 28  $\text{cm}^3$  of propene was bubbled into 40.0  $\text{cm}^3$  of 0.0200  $\text{mol dm}^{-3}$  acidified  $\text{KMnO}_4(\text{aq})$ . The resulting solution was titrated against  $\text{Fe}^{2+}(\text{aq})$  of concentration 0.0750  $\text{mol dm}^{-3}$ .

- (i) State the colour change at endpoint for this titration. [1]

**Pink/red-brown to colourless/yellow**

- (ii) Given that 5 moles of  $\text{Fe}^{2+}$  react with 1 mole of  $\text{MnO}_4^-$ , determine the volume of  $\text{Fe}^{2+}(\text{aq})$  needed to reach endpoint. [3]

$$\text{No. of moles of propene} = \frac{28}{24000}$$

$$= 1.167 \times 10^{-3} \text{ mol}$$

$$\text{No. of moles of } \text{MnO}_4^- \text{ reacted with propene} = \frac{1.167 \times 10^{-3}}{5} \times 2$$

$$= 4.667 \times 10^{-4} \text{ mol}$$

$$\text{No. of moles of } \text{MnO}_4^- \text{ originally} = \frac{40.0}{1000} \times 0.0200$$

$$= 8.000 \times 10^{-4} \text{ mol}$$

$$\begin{aligned}\text{No. of moles of MnO}_4^- \text{ left} &= 8.000 \times 10^{-4} - 4.667 \times 10^{-4} \\ &= 3.333 \times 10^{-4} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{No. of moles of Fe}^{2+} &= 3.333 \times 10^{-4} \times 5 \\ &= 1.667 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Volume of Fe}^{2+} &= \frac{1.667 \times 10^{-3}}{0.0750} \times 1000 \\ &= 22.2 \text{ cm}^3\end{aligned}$$

- (e) A mixture of propene ( $M_r = 42.0$ ) and 2-bromopropane ( $M_r = 122.9$ ) kept in a vessel of volume of  $3.60 \text{ dm}^3$  maintained at  $75^\circ\text{C}$  exerts a pressure of  $1.66 \times 10^5 \text{ Pa}$ . The mole fraction of propene in the mixture is 0.28.

Find the mass of the mixture of gases. [3]

[Total: 20]

$$\begin{aligned}\text{Average } M_r &= 0.28 \times 42.0 + (1 - 0.28) \times 122.9 \\ &= 100.2\end{aligned}$$

$$pV = \frac{m}{M_r}RT$$

$$\begin{aligned}m &= \frac{pVM_r}{RT} \\ &= \frac{1.66 \times 10^5 \times 3.60 \times 10^{-3} \times 100.2}{8.31 \times (75 + 273)} \\ &= 20.7 \text{ g}\end{aligned}$$

- 2 Copper is a transition metal, and is one of the metals used to make coins, along with silver and gold. Most copper is used in electrical equipment such as wiring and motors. It also has uses in construction and industrial machinery.

(a) One of the characteristic properties of copper is its ability to form coloured aqueous complexes shown in Fig 2.1.

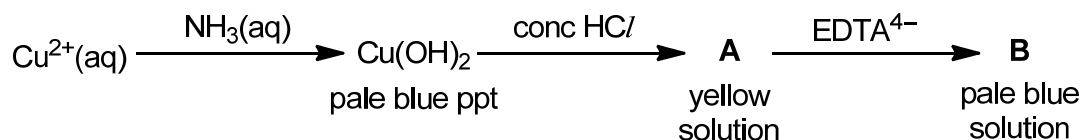
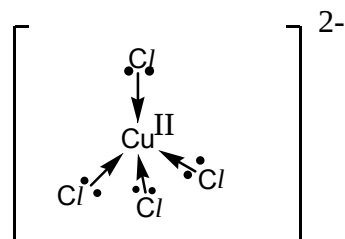


Fig. 2.1

- (i) State the complex ion **A**. [1]



- (ii) Draw the structure of complex ion **A**. [2]



- (iii)  $\text{EDTA}^{4-}$  is a hexadentate ligand. Deduce the formula of the complex ion **B**. [1]



- (iv) Suggest why complex **B** is readily formed from complex **A**. [1]

$[\text{Cu}(\text{EDTA})]^{2-}$  is more stable as compared to  $[\text{CuCl}_4]^{2-}$ , therefore  $\text{Cl}^-$  ligands will be displaced by the stronger  $\text{EDTA}^{4-}$  ligands. OR  $\text{EDTA}^{4-}$  is a stronger ligand than  $\text{Cl}^-$ .

- (v) Explain why aqueous  $\text{Cu}^{2+}$  ions are blue in colour. [3]

When ligands approach/are attached/bonded to the copper ion, they will cause the incompletely/ partially-filled/ $3d^9$  degenerate d-orbitals to split into two slightly different energy levels, d and  $d^*$  [OR] two groups of non-degenerate d-orbitals with small energy gap.

When electrons from the lower lying d-orbitals absorbs energy (orange colour) in the visible light region, it will be excited to the higher energy  $d^*$  orbital. This is known as d-d\* electronic transition.

The complementary colours, which is not absorbed which is blue is seen/ the colour observed is complementary to the colour that is absorbed.

- (vi) The numerical value of the solubility product,  $K_{sp}$  of  $\text{Cu}(\text{OH})_2$  is  $2.20 \times 10^{-20}$  at  $25^\circ\text{C}$ . Write the expression for  $K_{sp}$  and state its units. Calculate the solubility of  $\text{Cu}(\text{OH})_2$  at  $25^\circ\text{C}$ . [3]



$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^{-}]^2$$

$$\text{Units: mol}^3 \text{ dm}^{-9}$$

Let the solubility of  $\text{Cu}(\text{OH})_2$  be  $x \text{ mol dm}^{-3}$

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^{-}]^2 = x(2x)^2$$

$$2.20 \times 10^{-20} = 4x^3$$

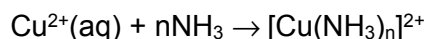
$$x = 1.77 \times 10^{-7} \text{ mol dm}^{-3}$$

- (b) When an aqueous solution of ammonia is shaken with an organic solvent, trichloromethane, at room temperature, the following equilibrium is set up between the two immiscible liquids.



The equilibrium constant,  $K_c$ , for this reaction is 0.04.

Water that is contaminated with copper(II) sulfate is harmful to crops, animals and humans. Some water that has been contaminated with  $0.100 \text{ mol dm}^{-3}$  copper(II) sulfate was allowed to reach dynamic equilibrium at room temperature with an excess of ammonia and trichloromethane. The aqueous layer was found to contain  $0.660 \text{ mol dm}^{-3}$  of ammonia, some of which reacted with  $\text{Cu}^{2+}(\text{aq})$  according to the following equation



The organic layer contained  $0.0104 \text{ mol dm}^{-3}$  of ammonia.

- (i) Define the term *dynamic equilibrium*. [1]  
**Dynamic equilibrium refers to a reversible reaction in which the forward rate of reaction is equal to the reverse rate of reaction. There is no net change in the concentrations of the reactants and the products.**
- (ii) Explain the relative solubility of ammonia in water and trichloromethane in terms of the intermolecular forces involved. [2]

**Ammonia is able to form hydrogen bonding with water, which is much stronger than the permanent dipole-permanent dipole attractions with trichloromethane molecules. Due to the strong forces of attraction between ammonia and water molecules, ammonia is highly soluble in water.**

- (iii) Hence, in terms of the position of equilibrium, explain why the value of  $K_c$  for equilibrium 1 is relatively low. [1]

Therefore, the position of equilibrium lies largely to the left and  $K_c$  for this reaction is relatively low.

- (iv) By calculating  $[\text{NH}_3(\text{aq})]$  present, show that the value of  $n$  in  $[\text{Cu}(\text{NH}_3)_n]^{2+}$  is 4. [2]

$$0.04 = \frac{[\text{NH}_3(\text{organic})]}{[\text{NH}_3(\text{aqueous})]}$$

$$0.04 = \frac{0.0104}{[\text{NH}_3(\text{aqueous})]}$$

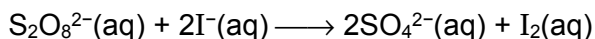
$$[\text{NH}_3(\text{aqueous})] = \frac{0.0104}{0.04} = 0.26 \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{Concentration of NH}_3 \text{ which reacted with Cu}^{2+}(\text{aq}) &= 0.660 - 0.26 \\ &= 0.40 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{Mol ratio of Cu}^{2+} : \text{NH}_3 &= 0.100 : 0.400 = 1 : 4 \\ n \text{ is } &4. \end{aligned}$$

- (c) Another characteristic property of transition metal ion is its ability to catalyse reactions.

The rate of the reaction between iodide and peroxodisulfate(VI) ions

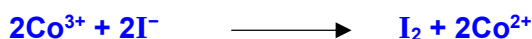


is very slow. If a small amount of aqueous transition metal, cobalt(II) ions is added to the mixture, the rate of reaction increases.

- (i) By considering relevant half equations from the *Data Booklet*, construct chemical equations to show how cobalt(II) ions behave as a catalyst in this reaction. No calculation is required. [2]



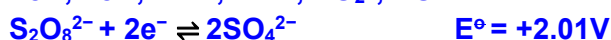
catalyst



catalyst regenerated

- (ii) Suggest another transition metal ion, which will be able to catalyse this reaction. [1]

$\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{VO}_2^+$ ,  $\text{VO}^{2+}$ .

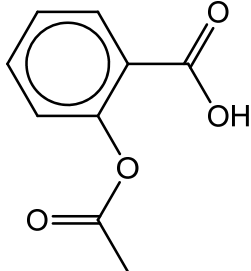
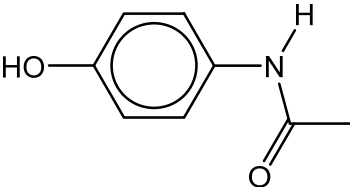


(Transition metal ion redox system requires a  $E^\circ$  of between +0.54V and +2.01V.)

[Total: 20]

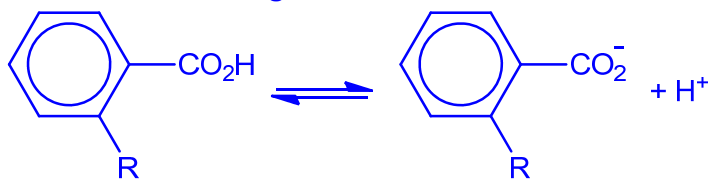
- 3 (a) Analgesics are medicines used to relieve pain. The two most common analgesics in the market are aspirin and paracetamol. Their structures and corresponding  $pK_a$  values are shown in Table 3.1.

Table 3.1

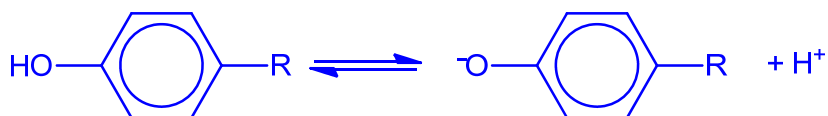
| Name of analgesic | Structure                                                                          | $pK_a$ value |
|-------------------|------------------------------------------------------------------------------------|--------------|
| Aspirin           |   | 3.49         |
| Paracetamol       |  | 10.30        |

- (i) Explain the difference in the  $pK_a$  values between aspirin and paracetamol. [2]

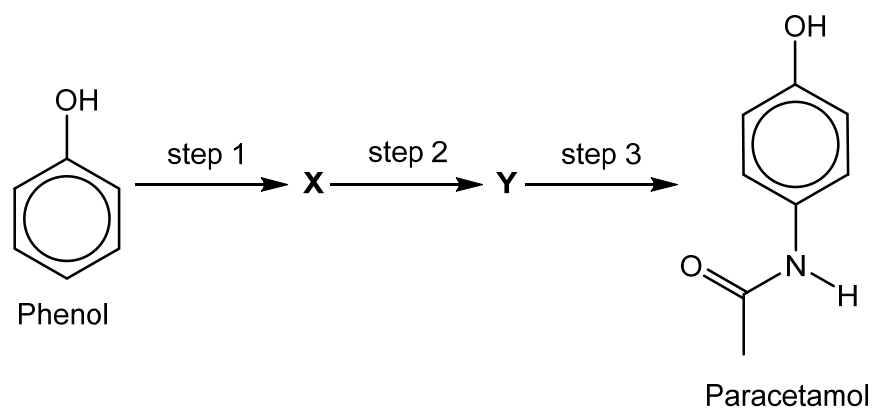
Aspirin is a stronger acid than paracetamol (due to its lower  $pK_a$  value) because in the carboxylate ion of aspirin, the negative charge on oxygen atom can be delocalised to a greater extent over the C atom and both O atoms. Hence the carboxylate ion is more resonance-stabilised. Position of equilibrium lies more to the right and aspirin dissociates to a larger extent.



For the phenoxide ion of paracetamol, the negative charge is only delocalised into the benzene ring and hence is less stable. Hence position of equilibrium lies less to the right and paracetamol dissociates to a smaller extent compared to that of Aspirin.

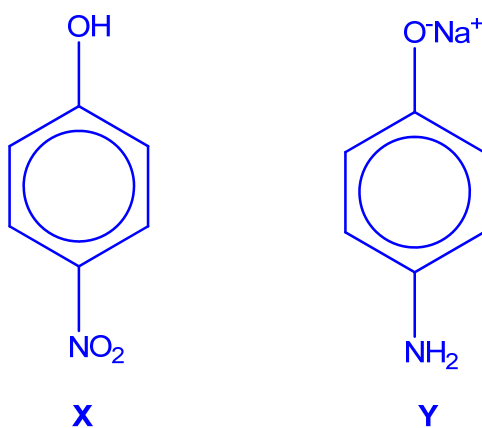


Paracetamol can be synthesised from phenol in a 3-step process shown in Fig 3.1.



**Fig. 3.1**

(ii) Suggest the structures for intermediates **X** and **Y**. [2]



(iii) Suggest the reagents and conditions required for step 1 to 3. [3]

**Step 1: dilute  $\text{HNO}_3$**

**Step 2: 1. Sn, conc  $\text{HCl}$ , heat under reflux; 2.  $\text{NaOH}$  (aq)**

**Step 3:  $\text{CH}_3\text{COCl}$**

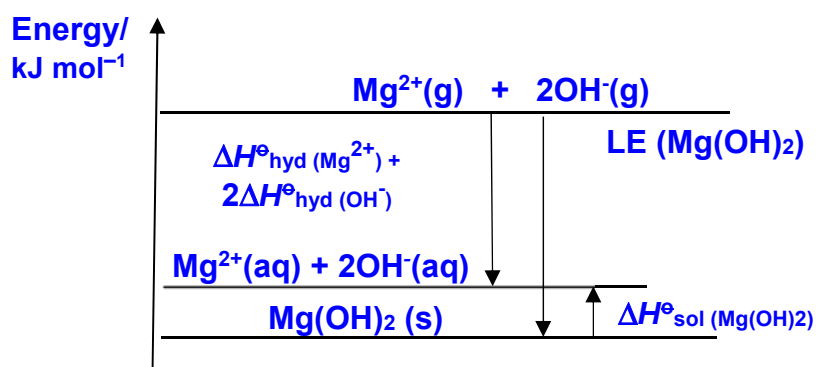
- (b) The use of aspirin has been shown to increase the risk of gastrointestinal bleeding. Hence buffering agents are added to aspirin to mitigate the problem of gastrointestinal bleeding. These buffering agents work by preventing the aspirin from concentrating in the walls of the stomach. Common buffering agents used include magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , and calcium carbonate,  $\text{CaCO}_3$ .

Some relevant standard enthalpy change of hydration values and lattice energy of  $\text{Mg}(\text{OH})_2$ , are shown in Table 3.2.

**Table 3.2**

| Enthalpy term                                                       | Value / $\text{kJ mol}^{-1}$ |
|---------------------------------------------------------------------|------------------------------|
| Standard enthalpy change of hydration of $\text{Mg}^{2+}(\text{g})$ | -1926                        |
| Standard enthalpy change of hydration of $\text{OH}^{-}(\text{g})$  | -460                         |
| Lattice energy of $\text{Mg}(\text{OH})_2(\text{s})$                | -2998                        |

Using relevant data in the table above, construct an energy level diagram to determine the standard enthalpy change of solution,  $\Delta H_{\text{sol}}^{\ominus}$ , of  $\text{Mg}(\text{OH})_2$  in water. [3]

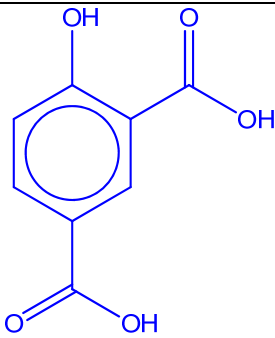


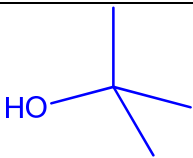
$$\begin{aligned}
 \Delta H_{\text{sol}} &= -\text{lattice energy} + \Sigma \Delta H_{\text{hyd}} \\
 &= -(-2998) + (-1926 - 2 \times 460) \\
 &= +152 \text{ kJ mol}^{-1}
 \end{aligned}$$

- (c) Compound **A** is an unsaturated ester containing a benzene ring and has a molecular formula of  $C_{16}H_{22}O_3$ . **A** reacts with neutral  $FeCl_3$  to give violet colouration. **A** reacts with  $H_2$  in the presence of Ni to produce compound **B** ( $C_{16}H_{24}O_3$ ). **B** exhibits enantiomerism whereas **A** does not.

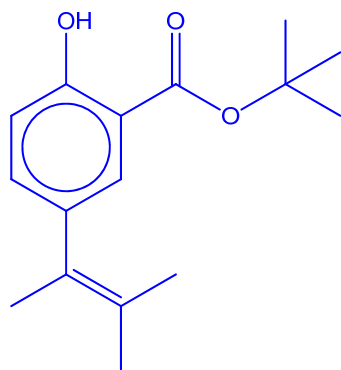
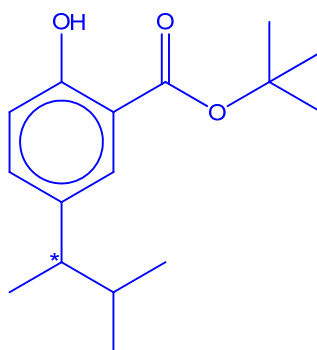
On heating with acidified  $KMnO_4$ , **A** gives three organic products, **C**,  $C_8H_6O_5$ , **D**,  $C_4H_{10}O$  and propanone ( $CH_3COCH_3$ ). 1 mole of **C** reacts with excess  $PCl_5$  to produce 2 moles of  $HCl$ . Effervescence is observed when a small piece of sodium metal is added to **D**.

Suggest the structures for **A** to **D** and explain the reactions described. [10]

| Observation/data                                                                                                                                             | Type of reaction                                                               | Deduction                                                                                                                                                                                                          | Structure                                                                                                                         |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|
| <b>A</b> reacts with neutral $FeCl_3$ to give violet colouration.                                                                                            | -                                                                              | <b>A</b> is a phenol/ contains a phenolic group.                                                                                                                                                                   | -                                                                                                                                 |
| <b>A</b> reacts with $H_2$ in the presence of Ni to produce compound <b>B</b> ( $C_{16}H_{24}O_3$ ).                                                         | catalytic addition/<br>reduction of $C=C$ bond                                 | <b>A</b> is likely to contain <u>only one <math>C=C</math> bond</u> since there is an addition of 2 H atoms in <b>B</b> .                                                                                          | -                                                                                                                                 |
| <b>B</b> exhibits enantiomerism whereas <b>A</b> does not.                                                                                                   | -                                                                              | <b>B</b> contains a <u>chiral carbon</u> whereas <b>A</b> does not.                                                                                                                                                | -                                                                                                                                 |
| On heating with acidified $KMnO_4$ , <b>A</b> gives three organic products, <b>C</b> , $C_8H_6O_5$ , <b>D</b> , $C_4H_{10}O$ and propanone ( $CH_3COCH_3$ ). | Acidic hydrolysis of ester,<br><br>oxidative cleavage and side-chain oxidation | Hydrolysis of ester occurred to form a <u>carboxylic acid and an alcohol</u> .<br><br>There is side chain oxidation on the benzene ring since there is <u>loss of 1 C atom</u> (or formation of 1 mol of $CO_2$ ). | -                                                                                                                                 |
| 1 mole of <b>C</b> reacts with excess $PCl_5$ to produce 2 moles of $HCl$ .                                                                                  | Nucleophilic substitution of $-OH$ group                                       | <b>C</b> is likely to contain a benzene ring with <u>2 carboxylic acid groups</u> and 1 phenol group.                                                                                                              |  <p style="text-align: center;"><b>C</b></p> |

|                                                                                     |                |                                                                                                         |                                                                                                                                 |
|-------------------------------------------------------------------------------------|----------------|---------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|
| Effervescence is observed when a small piece of sodium metal is added to <b>D</b> . | Redox reaction | <b>D</b> is likely to be a <u>tertiary alcohol</u> since it is not oxidised by acidic $\text{KMnO}_4$ . |  <p style="text-align: center;"><b>D</b></p> |
|-------------------------------------------------------------------------------------|----------------|---------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|

Hence structures of **A** and **B** are

**A****B**

[Total: 20]

## Section B

Answer **one** question from this section.

- 4 (a) The decomposition of calcium and magnesium carbonates has industrial application as flame retardants due to the endothermic nature of these reactions.

- (i) Write an equation showing the thermal decomposition of calcium carbonate. [1]

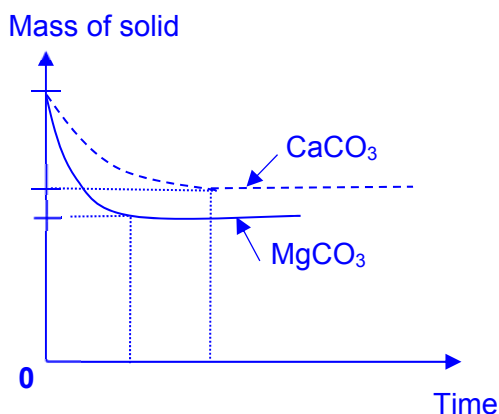


- (ii) Compare and explain the decomposition temperature of calcium and magnesium carbonates. [3]

$\text{CaCO}_3$  decomposes at a higher temperature as compared to  $\text{MgCO}_3$ . This is because  $\text{Ca}^{2+}$  has a larger ionic radius than  $\text{Mg}^{2+}$ , and a lower charge density. Thus  $\text{Ca}^{2+}$  polarises the carbonate ion to a lesser extent hence the C-O bonds are stronger which require higher temperature to break.

- (iii) Separate samples of calcium carbonate and magnesium carbonate of the same mass, were decomposed completely under constant heating and the variation of the masses of the two samples were measured.

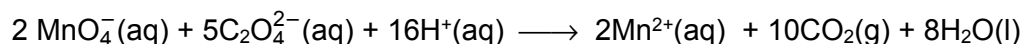
Sketch a graph of the mass of solid against time for the two separate samples, indicating clearly the time when decomposition was complete and the final mass for each sample. No calculations are required. [2]



- (iv) Besides absorption of heat to slow down the spread of a flame, suggest another reason why  $\text{CaCO}_3$  acts as a flame retardant. [1]

$\text{CO}_2$  released can displace the oxygen required for a combustion.

- (b) One way to study reaction mechanisms is to deduce the rate equation from kinetics experiments, such as that for the redox reaction between manganate (VII) ions and ethanedioate ions.



A study of the kinetics of this reaction was carried with a suitable catalyst and with  $[\text{C}_2\text{O}_4^{2-}]$  at  $2.00 \text{ mol dm}^{-3}$  and data collected are shown in Table 4.1

**Table 4.1**

| time / min | $[\text{MnO}_4^-] / \text{mol dm}^{-3}$ |
|------------|-----------------------------------------|
| 0          | 0.0200                                  |
| 3          | 0.0160                                  |
| 6          | 0.0128                                  |
| 9          | 0.0104                                  |
| 12         | 0.0084                                  |
| 15         | 0.0068                                  |
| 18         | 0.0056                                  |

- (i) Plot the data on suitable axes, using the graph paper provided. [2]
- (ii) Use your graph to determine the order of reaction with respect to  $[\text{MnO}_4^-]$ , showing your working clearly including construction lines on your graph. [2]
- (iii) Given that the reaction is first order with respect to  $[\text{C}_2\text{O}_4^{2-}]$ , give the rate equation for the reaction. [1]
- (iv) Determine the initial rate from the graph and use it, together with your rate equation, to calculate the rate constant for the reaction, stating its units. [2]
- (v) Without the initial addition of the catalyst, the reaction is initially slow then speeds up due to autocatalyst,  $\text{Mn}^{2+}$ , produced, and finally slows down due to low concentration of reactants remaining.

Sketch a graph  $[\text{MnO}_4^-]$  against time if the experiment was repeated without the initial addition of catalyst. [1]

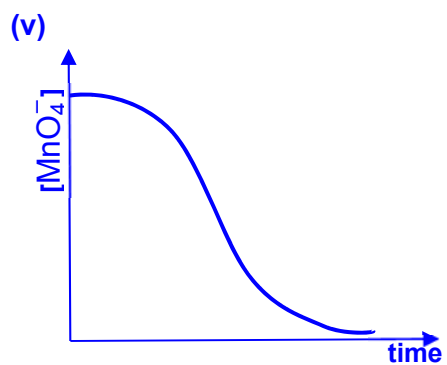
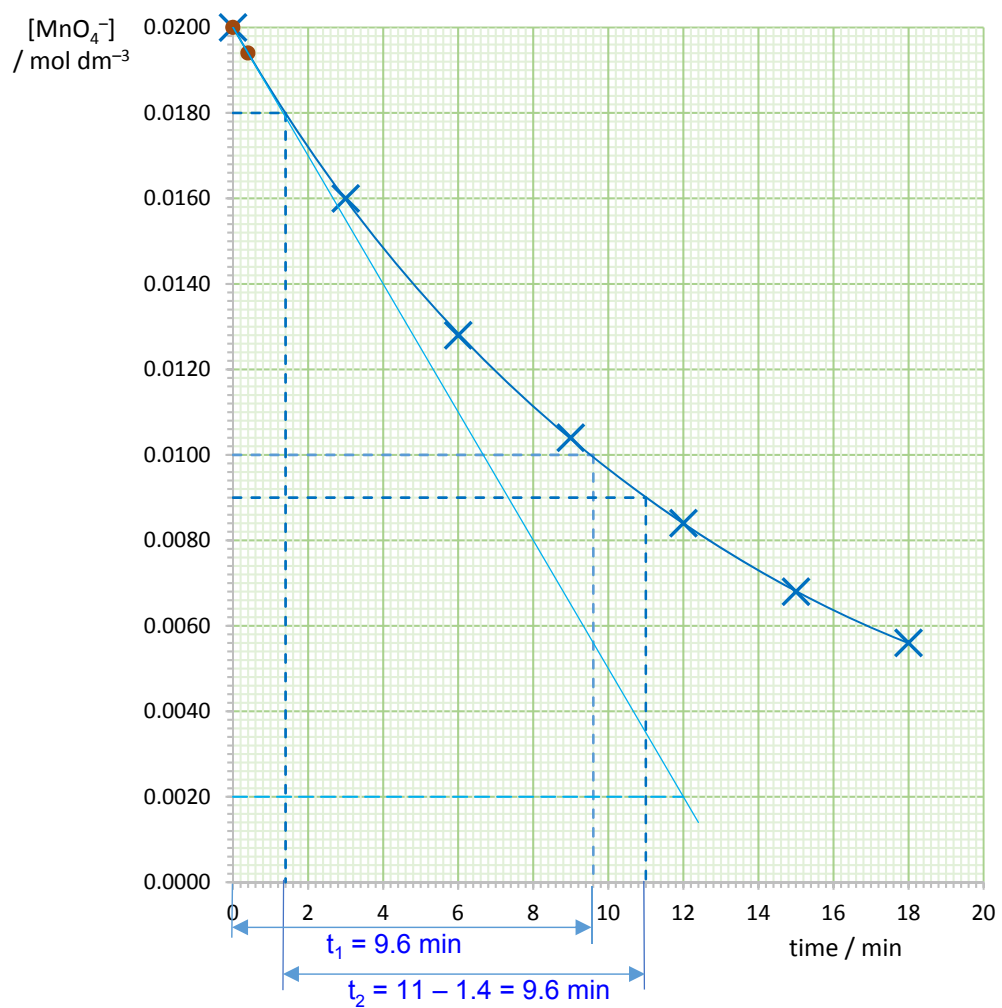
- (ii) **Using half-lives,**  
 **$1^{\text{st}}$  half-life =  $2^{\text{nd}}$  half-life = 9.6 min**

**Since both half-lives are constant, the order of reaction with respect to  $[\text{MnO}_4^-]$  is 1.**

- (iii) **rate =  $k [\text{C}_2\text{O}_4^{2-}] [\text{MnO}_4^-]$**

- (iv) **rate =  $-\frac{0.0200 - 0.0020}{0 - 12}$**   
**=  $0.00150 \text{ mol dm}^{-3} \text{ min}^{-1}$**

$$k = \frac{\text{rate}}{[\text{C}_2\text{O}_4^{2-}][\text{MnO}_4^-]} = \frac{0.00150}{2.00 (0.0200)} = \mathbf{0.0375 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}}$$



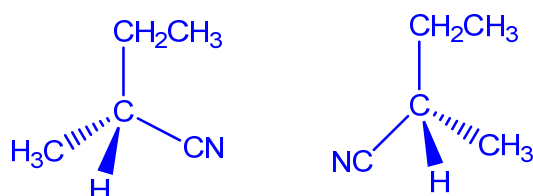
- (c) Another way to study reaction mechanisms is to make deductions from the ease of obtaining the products as well as the identity of products formed.

2-bromobutane undergo nucleophilic substitution with nitrile,  $\text{CN}^-$ , relatively faster, as compared to the reaction of 2-chlorobutane with nitrile,  $\text{CN}^-$ .

- (i) Under suitable conditions, an initially optically pure (only one enantiomer) sample of 2-bromobutane can undergo reaction with  $\text{CN}^-$ , and produce a mixture which is almost optically inactive.

Name the mechanism that has taken place for this, and give the structures of the products formed. [2]

**Mechanism: Nucleophilic substitution reaction ( $\text{S}_{\text{N}}1$ )**



- (ii) A suitable condition for the reaction in (i) can be the use of neutral **polar** solvent (e.g. propanone) instead of non-polar solvents. Suggest why this is the case in consideration of the mechanism stating clearly the interactions involved. [1]

**Polar solvents can help to stabilise the carbocation formed, due to the ion-dipole interactions between the carbocation and polar solvent molecules, which allows the reaction to proceed via  $\text{S}_{\text{N}}1$  mechanism.**

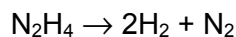
- (iii) Explain why 2-chlorobutane reacts more slowly with nucleophiles, relating to the steps in the mechanism in (i). Quote relevant values from the *Data Booklet* to substantiate your answer. [2]

**$\text{BE (C-C)} = 340 \text{ kJ mol}^{-1}$ ;  $\text{BE (C-Br)} = 280 \text{ kJ mol}^{-1}$**

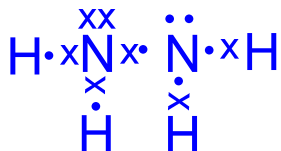
**The C-C bond is stronger than C-Br bond, and the breaking of this bond is involved in the slow or rate-determining step (required if  $\text{S}_{\text{N}}1$  given in (i)), hence the reaction is slower with 2-chlorobutane**

[Total: 20]

- 5 (a) The decomposition of hydrazine,  $\text{N}_2\text{H}_4$ , can be used to produce  $\text{H}_2$  gas as shown in the following reaction.



- (i) Draw a dot-and-cross diagram showing the bonding in  $\text{N}_2\text{H}_4$ . [1]



- (ii) Use your diagram to suggest the shape of  $\text{N}_2\text{H}_4$  about nitrogen atom. [1]  
**Trigonal pyramidal**
- (iii) Use your diagram to suggest the bond angle about N atom in  $\text{N}_2\text{H}_4$ . [1]  
 **$107^\circ$**
- (i) The boiling points of hydrazine, nitrogen and ammonia are shown in Table 5.1

**Table 5.1**

| compound               | boiling point/ $^\circ\text{C}$ |
|------------------------|---------------------------------|
| $\text{N}_2\text{H}_4$ | 114                             |
| $\text{NH}_3$          | -33                             |
| $\text{N}_2$           | -196                            |

Suggest an explanation for the difference in boiling points of these three compounds. [4]

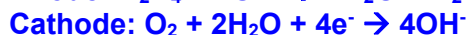
**All three compounds have simple molecular structures.**

**The hydrogen bonding between  $\text{NH}_3$  molecules is stronger than the instantaneous dipole-induced dipole (id-id) attraction between  $\text{N}_2$  molecules. Greater amount of energy required to overcome the intermolecular H-bonding in  $\text{NH}_3$  than the intermolecular id-id in  $\text{N}_2$ . Thus, boiling point of  $\text{NH}_3$  is higher.**

**The hydrogen bonding between hydrazine molecules is more extensive (2 hydrogen bonds per molecule) than between  $\text{NH}_3$  molecules (1 hydrogen bond per molecule). Greater amount of energy required to overcome the more extensive intermolecular Hydrogen bonding in hydrazine molecules than in  $\text{NH}_3$ . Thus, boiling point of hydrazine is higher.**

- (b) Hydrazine can be used in a fuel cell to generate electricity. At the anode, nitrogen gas is produced from hydrazine in alkaline medium. At the cathode, oxygen gas is being supplied into water.

- (i) Construct half equations for the anode and cathode reactions. [2]



- (ii) Hence, write the overall equation. [1]



- (iii) The cell is capable of producing an e.m.f. of 1.56 V under standard conditions. By using suitable data from the *Data Booklet*, suggest a value of the  $E^\circ$  of the anode. [1]

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{oxi}}$$

$$1.56 = +0.40 - E^\circ_{\text{oxi}}$$

$$E^\circ_{\text{oxi}} = -1.16 \text{ V}$$

- (iv) Calculate  $\Delta G$  for the reaction. [1]

$$\Delta G = -nFE^\circ_{\text{cell}}$$

$$= - \frac{4 \times 96500 \times 1.56}{1000}$$

$$= -602 \text{ kJ mol}^{-1}$$

- (v) State one possible advantage of using fuel cell compared to burning hydrocarbons in car engines. [1]

**It is pollution free. (only harmless/inert gases are produced, in this case,  $\text{H}_2\text{O}$  and  $\text{N}_2$ )**

**It has a high power to mass ratio.**

**It is highly efficient.**

- (c) Local anesthesia is used in surgeries where it is applied to numb the feelings of a specific part of a body. Lidocaine and procaine are examples of local anesthesia shown in Fig 5.1

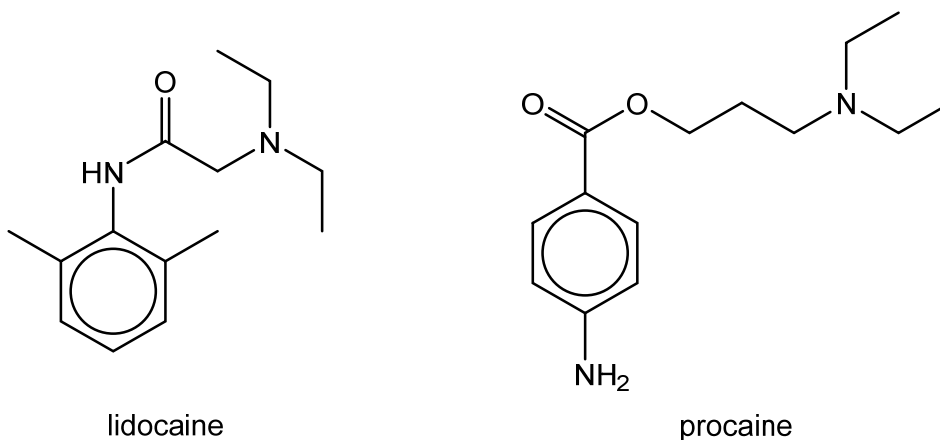


Fig. 5.1

The final step of the synthesis of lidocaine is shown in Fig 5.2.

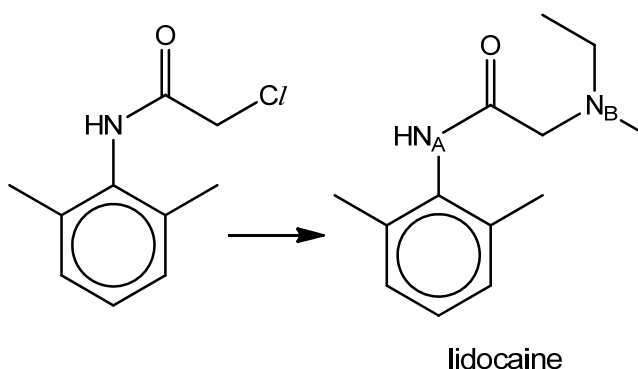
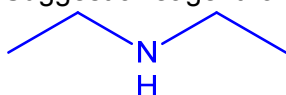


Fig. 5.2

- (i) Suggest a reagent for the above reaction. [1]



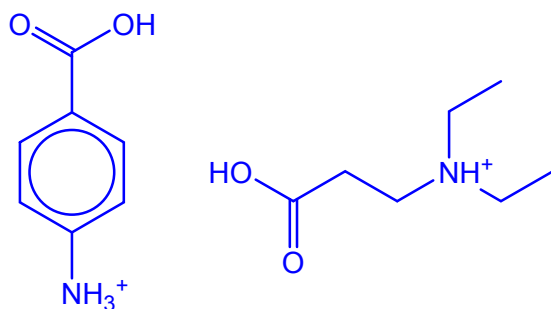
- (ii) Suggest how the basicity of  $N_A$  might compare to that of  $N_B$ . Give reasons for your answers. [2]

$N_A$  is less basic than  $N_B$  due to the lone pair of electrons on nitrogen atom in the amide bond is being delocalised into the  $C=O$  group, making it less available to accept a proton.

- (iii) A possible single chemical test to distinguish procaine and lidocaine involves the use of acidified potassium dichromate. Explain the chemistry involved, including any observation. Draw the structures of the products for the positive test. [3]

Hydrolysis of ester or amide bond, followed by oxidation of alcohol formed of procaine.

Orange potassium dichromate turns green with procaine.



- (iv) Suggest another reagent that can also be used to distinguish between lidocaine and procaine. [1]

Aqueous bromine/ bromine in hexane

[Total: 20]