## Section A

#### Answer **all** questions in the spaces provided.

- 1 (a) Calcium ethanedioate, CaC<sub>2</sub>O<sub>4</sub>, is a white needle–like crystalline solid. When a pure sample of anhydrous CaC<sub>2</sub>O<sub>4</sub> was heated strongly at 400 °C until no further change in mass is observed, a white solid **B** and 0.028 g of carbon monoxide gas were obtained as the only products.
  - (i) Given that 1 mole of  $CaC_2O_4$  decomposes to give 1 mole of CO(g), write a balanced equation for the thermal decomposition of  $CaC_2O_4$  and identify solid **B**.

equation :  $CaC_2O_4 \longrightarrow CaCO_3 + CO$ Solid **B** :  $CaCO_3$ 

(ii) Hence, determine the mass of **B** obtained in the reaction.

Moles of of CaCO<sub>3</sub> = moles of CO =  $\frac{0.028}{28.0}$  = 0.0010 mol

Mass of CaCO<sub>3</sub> obtained =  $0.0010 \times 100.0 = 0.10 \text{ g}$ 

[3]

(b) The formula of potassium hydrogen ethanedioate can be written as  $K_x H_y (C_2 O_4)_z$ . In an experiment to determine the values of *x*, *y* and *z*, 4.50 g of this compound was dissolved in water and the solution made up to 1 dm<sup>3</sup>.

20.0 cm<sup>3</sup> of the solution was pipetted into a conical flask and then titrated with 0.0200 mol dm<sup>-3</sup> KMnO<sub>4</sub> in an acidic medium. It was found that 16.50 cm<sup>3</sup> of KMnO<sub>4</sub>(aq) was needed for the complete reaction with ethanedioate ions, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, present. During the titration, effervescence of carbon dioxide is produced.

Given the reaction of manganate(VII) in acidic medium as:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

(i) Write a balanced half–equation for the reaction of  $C_2O_4^{2-}$  during titration.

half-equation :  $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^{-1}$ 

(ii) Calculate the mass of  $C_2O_4^{2-}$  present in 1 dm<sup>3</sup> of the solution.

E.c.f. if half-equation from (i) is wrong.

Overall equation:  $5C_2O_4^{2-} + 2MnO_4^{-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$ 

Moles of  $C_2 O_4^{2-}$  in 20.0 cm<sup>3</sup> =  $\frac{5}{2} \times (0.0200 \times \frac{16.50}{1000})$ 

$$= 8.25 \times 10^{-4}$$
 mol

Mass of  $C_2 O_4^{2-}$  in 1000 cm<sup>3</sup> =  $(8.25 \times 10^{-4}) \times 88.0 \times \frac{1000}{20}$ 

## = <u>3.63 g</u>

(iii) Given that 4.50 g of potassium hydrogen ethanedioate contains 0.060 g of hydrogen, calculate the mass of potassium present in the sample.

Mass of potassium present = 4.50 - 0.060 - 3.63 = 0.81 g

(iv) Hence, determine the values *x*, *y* and *z*.

	K	Н	C <sub>2</sub> O <sub>4</sub>
Mass / g	0.81	0060	3.63
Moles / mol	0.81/ 39.1	0.060/1.0	3.63/88.0
	= 0.021	= 0.060	= 0.041
Ratio	1	3	2

Working to calculate moles of all species:

<u>x = 1</u>, <u>y = 3</u> and <u>z = 2</u>

Formula is  $KH_3(C_2O_4)_2$ .

[6]

[Total: 9]

**2** The following table lists the standard enthalpy changes of combustion,  $\Delta H_c^{\ominus}$ , of some monohydric alcohols.

alcohol	$\Delta H_{c}^{\ominus}$ / kJ mol <sup>-1</sup>
methanol(l)	-715
ethanol(l)	-1367
propan-1-ol(l)	?
butan-1-ol(l)	-2671

(a) Write an equation to represent the standard enthalpy change of combustion of propan-1- ol.

$$CH_3CH_2CH_2OH(l) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

[1]

(b) (i) The difference in the standard enthalpy change of combustion of methanol and ethanol is  $-652 \text{ kJ mol}^{-1}$ . By considering the structures of the two alcohols, suggest the significance of this difference.

The difference corresponds to the enthalpy change of combustion of a  $-CH_2$ -group.

(ii) Hence suggest a value of  $\Delta H_c^{\ominus}$  for propan-1-ol.

Suggest a value of  $\Delta H_c^{\ominus}$  for propan–1–ol : –2019 kJ mol<sup>-1</sup>

(iii) Given that  $\Delta H_{f}^{\ominus}[H_{2}O(l)] = -286 \text{ kJ mol}^{-1}$  and  $\Delta H_{f}^{\ominus}[CO_{2}(g)] = -394 \text{ kJ mol}^{-1}$ , and using your answer to (b)(ii), calculate the standard enthalpy change of formation of propan-1-ol,  $\Delta H_{f}^{\ominus}[CH_{3}CH_{2}CH_{2}OH(l)]$ .

 $\Delta H_{c}^{\ominus}[CH_{3}CH_{2}CH_{2}OH(l)] = 3 \Delta H_{f}^{\ominus}[CO_{2}(g)] + 4 \Delta H_{f}^{\ominus}[H_{2}O(l)] - \Delta H_{f}^{\ominus}[CH_{3}CH_{2}CH_{2}OH(l)] - 2019 = [3(-394) + 4(-286)] - \Delta H_{f}^{\ominus}[CH_{3}CH_{2}CH_{2}OH(l)] - \Delta H_{f}^{\ominus}[CH_{3}CH_{2}CH_{2}OH(l)] = -307 \text{ kJ mol}^{-1}$ 

[4]

(c) Ethanol is metabolised in the body by an *enzyme* called alcohol dehydrogenase. Define *enzyme* and describe how alcohol dehydrogenase affects the rate of ethanol metabolism in the body.

An enzyme is a biological catalyst that **speeds up** */* **alters** the rate of chemical reactions and remained chemically unchanged at the end of reaction.

An enzyme provides an alternate pathway with **lower**  $E_a$  for reactions to take place. Through the formation of an enzyme–substrate complex, an enzyme increases the likelihood of <u>correct geometry</u> for reactions to occur. **3 (a)** Below is the incomplete sketch of the plot of first ionisation energies against atomic (proton) numbers for ten elements.



- (i) On the diagram above, use crosses (x) to mark the first ionisation energies of Si and S.
- (ii) Explain why the first ionisation energy of potassium is lower than that of sodium.

The valence electron of potassium is located in a shell with a higher principal quantum number. Hence the valence electrons are further away from the nucleus and less strongly attracted to the nucleus. Smaller amount of energy is needed to remove the valence electron from K.

(iii) State which of the ten elements is likely to have the lowest second ionisation energy and write an equation to represent the second ionisation energy of this element.

 $\begin{array}{l} \text{Calcium} \\ \text{Ca}^{\text{\tiny +}}(g) + e \rightarrow \text{Ca}^{2\text{\tiny +}}(g) \end{array}$ 

[4]

(b) X, Y and Z are elements in Period 3 of the Periodic Table. The oxide of X dissolves sparingly in water to give a weakly alkaline solution. The oxide of Y does not react with water, but reacts with both acids and bases. Z reacts with oxygen to form a covalent oxide with a very high melting point.

(i) Fill in the table below by identifying the elements **X**, **Y** and **Z** and suggest the pH of their chlorides in water.

	identity of element	pH of the chloride in water
Х	Mg	6.5
Y	Al	3
Z	Si	2

(ii) Write balanced chemical equations to show how oxide of **Y** reacts with both hydrochloric acid and calcium hydroxide.

 $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ 

 $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$ 

[4]

[Total: 8]

**4** Data concerning methanol and two of its analogues are given in the table below.

compound	Mr	atomic radius of atom Z in CH₃ZH / nm	dipole moment / D	boiling point / °C	$pK_a$ ( $pK_a = -log_{10}K_a$ )
CH₃OH	32.0	0.073	1.7	65	15.5
CH₃SH	48.1	0.102	1.5	6	10.4
CH₃SeH	95.0	0.116	1.3	25	≈ 5

No calculation is required.

- (a) Explain the differences in boiling points of the three compounds.
  - All three substances are simple molecular.
  - A larger amount of energy is needed overcome strong hydrogen bonding between CH<sub>3</sub>OH molecules than the weaker van der Waals' interactions between CH<sub>3</sub>SH or CH<sub>3</sub>SeH molecules.
  - Thus CH<sub>3</sub>OH has the highest boiling point.
  - Number of electrons in CH<sub>3</sub>SeH is larger than that in CH<sub>3</sub>SH.
    OR Size of electron cloud of CH<sub>3</sub>SeH is larger than that of CH<sub>3</sub>SH.
  - CH<sub>3</sub>SeH is more easily polarized than CH<sub>3</sub>SH.
  - A larger amount of energy is needed to overcome stronger and more significant van der Waals' interactions *OR* instantaneous induced dipole interactions between CH<sub>3</sub>SeH molecules.
  - Thus CH<sub>3</sub>SeH has a higher boiling point than CH<sub>3</sub>SH.

- (b) Arrange the three compounds in order of **decreasing** acidity and suggest a reason for this trend.
  - Strongest CH<sub>3</sub>SeH > CH<sub>3</sub>SH > CH<sub>3</sub>OH Weakest

(**Z** = O, S or Se)

- Size of atom decreases from Se to O.
- **Z**–H bond length decreases from Se–H to O–H.
- Bond strength increases from Se–H to O–H.
- Ease of breaking **Z**–H bond decreases from Se to O.

OR

- Size of atom decreases from Se to O.
- Charge density of conjugate base anion, **Z**<sup>-</sup>, increases from Se to O.
- Ease of Z<sup>-</sup> to accommodate the negative charge and hence the stability of Z<sup>-</sup> decreases from Se to O.

[2]

(c) When each of the three compounds has dissolved, each molecule is surrounded by water molecules. Draw simple diagrams to show how a water molecule interacts with a CH<sub>3</sub>SH molecule and with a CH<sub>3</sub>OH molecule. Label each diagram to show the type of interaction involved.



[2]

# [Total: 7]

**5** Three important natural–occurring compounds used as flavourings in the food industry are shown below:



(a) Describe two chemical tests which can be used to distinguish the three compounds.

Test 1: Add Fehling's reagent to all three compounds and warm. Only B will give a reddish–brown ppt of  $Cu_2O$  while A and C will not give any reddish–brown ppt.

Test 2: Add cold dilute alkaline KMnO<sub>4</sub>. C will decolourise purple KMnO<sub>4</sub> while A will not decolourise purple KMnO<sub>4</sub>.

Accept Br<sub>2</sub>(aq) at r.t. / Tollens' reagent and warm for Test 2.

[3]

(b) Give two reasons to explain whether compound **C** can exhibit geometric isomerism.

C is unable to exhibit geometric isomerism.

- 1. One of the C atoms of the acyclic C=C bond has the same substituent.
- 2. The cyclic ring is too small to allow the alkyl groups of the cyclic C=C bond to be on opposite side.

OR Trans isomer is energetically unfavourable due to the angle strain posed by the small 6–membered ring.

[2]

(c) Carvone can be converted to a common precursor **D** in a two-step synthesis for the making of synthetic flavourings.



Compound **D** 

State the reagents and conditions for each step and give the structure of the intermediate in the synthesis of  $\mathbf{D}$ .





[3]

## Section B

Answer any **two** questions from this section on separate answer paper.

- **1(a)** Simple esters are flammable liquids. Flammability is affected by volatility. Methyl ethanoate is an example of one such flammable liquid with a characteristically pleasant smell.
  - (i) Define the term standard enthalpy change of formation of methyl ethanoate.

It is the heat change when 1 mole of methyl ethanoate is formed from its constituent elements, under standard conditions. (298K, 1 atm).

(ii) Use the standard enthalpy changes of combustion,  $\Delta H_c^{\ominus}$  of some substances in the table shown below to calculate the standard enthalpy change of formation of methyl ethanoate.

Substance	Δ <i>H</i> <sub>c</sub> <sup>↔</sup> (298 K) /		
	kJ mol <sup>−1</sup>		
carbon	-394		
hydrogen	-286		
methyl ethanoate	-1592		

Equation for the formation of methyl ethanoate:

 $3C(s) + 3H_2(g) + O_2(g) \rightarrow CH_3COOCH_3(I)$ 

Using  $\Delta H_c^{\ominus}$  formula method,  $\Delta H_f^{\ominus}$  (methyl ethanoate) =  $\Sigma \Delta H_c^{\ominus}$  (prdts) –  $\Sigma \Delta H_c^{\ominus}$  (rxts) =  $3 \Delta H_c^{\ominus}$  (C) +  $3 \Delta H_c^{\ominus}$  (H<sub>2</sub>) –  $\Delta H_c^{\ominus}$  (methyl ethanoate) = 3(-394) + 3(-286) - (-1592)=  $-448 \text{ kJ mol}^{-1}$ 

(b) A student used the apparatus shown below in an attempt to determine the standard enthalpy change of combustion for ethyl ethanoate.

[3]



A preliminary experiment was carried out using methyl ethanoate. The ester was burned in a spirit burner underneath a copper can so that the flame from the burner heated 300 cm<sup>3</sup> of water in the can. It was found that 0.980 g of methyl ethanoate was required to raise the temperature of the water in the can by 10.0 °C.

(i) Using the  $\Delta H_c^{\ominus}$  value in (a)(ii), calculate the maximum heat released by mass of methyl ethanoate burned in the preliminary experiment. Hence, calculate the percentage of heat transferred to heat up the water in the can.

In your calculation, ignore the heat capacity of the copper can, and use the figure of  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$  for the specific heat capacity of water.

Moles of methyl ethanoate burned = 0.980/74.0 = 0.0132 mol

Maximum heat released =  $1592 \times 0.0132 = 21.0 \text{ kJ}$ 

Heat transferred to and absorbed by water =  $300 \times 4.18 \times 10 = 12540 \text{ J} = 12.5 \text{ kJ}$ 

Percentage efficiency or percentage of heat transferred =  $\frac{12.5}{21.0}$  x 100% = 59.5 %

(ii) When the experiment was repeated with ethyl ethanoate, the following results were obtained.

Mass of ethyl ethanoate burned = 0.948 g Increase in temperature of 300 cm<sup>3</sup> water = 11.5 °C

Using your answer in **(b)(i)** calculate the apparent(theorectical)  $\Delta H_c^{\ominus}$  of ethyl ethanoate.

[5]

Heat transferred to and absorbed by water = 300 x 4.18 x 11.5 = 14 421 J

Since the process is only 59.5 % efficient, apparent/theoretical heat released by ethyl ethanoate burned =  $\frac{100}{59.5}$  x 14 421 =24 237 J = 24.2 kJ Moles of ethyl ethanoate burned = 0.948/88.0 = 0.010773 mol

$$\Delta H_c^{\oplus}$$
 of ethyl ethanoate =  $-\frac{24.2}{0.010773}$  =  $-2250 \text{ kJ mol}^{-1}$  (3sf)

- (c) Methyl ethanoate can be prepared using methanol, CH<sub>3</sub>OH and ethanoic acid in the laboratory.
  - (i) Write an equation for the formation of methyl ethanoate using methanol and ethanoic acid. State the conditions required.

 $CH_3OH + CH_3COOH \iff CH_3COOCH_3 + H_2O$ 

Conditions: concentrated sulfuric acid, reflux

Methanol can be converted into ethanoic acid in a three-step synthesis as shown.

(ii) Suggest reagents and conditions for Steps 1, 2 and 3. State the intermediate compounds **P** and **Q** formed during the synthesis.

Step 1: PBr<sub>3</sub> or PCl<sub>3</sub> or PCl<sub>5</sub> (Substitution)

Step 2: alcoholic KCN, reflux (Substitution)

Step 3: dilute H<sub>2</sub>SO<sub>4</sub>, reflux (Acid hydrolysis)

Compound P : CH<sub>3</sub>Br or CH<sub>3</sub>Cl

Compound Q: CH<sub>3</sub>CN

(iii) State the oxidation number of carbon in methanol, CH<sub>3</sub>OH

- 2

(iv) Using only the elements C, H and O, draw the structural formulae of two compounds, A and B, each containing a single carbon atom with an oxidation number of 0 and +2 respectively.

A: HCHO B: HCOOH

(v) Suggest reagents and conditions for converting methanol into each of the two compounds **A** and **B**.

[10]

**A:**  $K_2Cr_2O_7$ , dilute sulfuric acid and heat with distillation **B:**  $K_2Cr_2O_7$  or KMnO<sub>4</sub> dilute sulfuric acid and heat

(d) Successive reactions of dihalgeno compounds are shown below. The following transformations show the different reactivities of the organic dihalogeno compound.

Suggest the structures of compounds **C** and **D**.





(i)

Draw a dot–and–cross diagram to show the bonding in the molecule of NO<sub>2</sub>.

(ii) The following diagram shows the shape of the  $NO_2^-$  ion.



Suggest a value for the O–N–O bond angle in the  $\mathrm{NO_2}^-$  ion and explain your answer.

Hence, suggest a value for the O–N–O bond angle in the  $NO_2$  molecule, giving reasons for your choice.

[5]

- Electron pair geometry for NO<sub>2</sub><sup>-</sup> is trigonal planar. Since lone pair bond pair repulsion > bond pair – bond pair repulsion, O–N–O bond angle for NO<sub>2</sub><sup>-</sup> is less than 120°.
- Suggested bond angle: e.g. 115° (Accept any value between 110° and 120°.)
- In NO<sub>2</sub> molecule, the single unpaired electron on N does not repel the neighbouring bond pairs as effectively as the lone pair on N in the NO<sub>2</sub><sup>-</sup> ion. Thus, O–N–O bond angle for NO<sub>2</sub> is expected to be more than that of NO<sub>2</sub><sup>-</sup> ion.
- Suggested bond angle: e.g. 135° (Accept any value between the bond angle of NO<sub>2</sub><sup>-</sup> and 170°.)
- (b) At room temperature, gaseous nitrogen dioxide and dinitrogen tetraoxide are in dynamic equilibrium according to the following equation:

 $N_2O_4(g) \implies 2NO_2(g) \qquad \Delta H = +58 \text{ kJ mol}^{-1}$ 

(i) State Le Chatelier's Principle.

If a system in equilibrium is subjected to a change which disturbs the equilibrium, the system responds in such a way so as to counteract the effect of the change.

- (ii) Use the Le Chatelier's Principle to deduce qualitatively the effect of increasing
  - I pressure II temperature

on the average molecular mass of a mixture of N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub>.

[5]

- When pressure increases, by Le Chatelier's Principle, equilibrium position shifts left to favour the side of the reaction with fewer moles of gas molecules.
- Proportion of N<sub>2</sub>O<sub>4</sub> in the mixture increases OR Proportion of NO<sub>2</sub> in the mixture decreases.
- Average *M*<sub>r</sub> of mixture increases.
- When temperature increases, by Le Chatelier's Principle, equilibrium position shifts right to favour the forward endothermic reaction to absorb the heat applied.
- Proportion of  $N_2O_4$  in the mixture decreases  $\overrightarrow{OR}$  Proportion of  $NO_2$  in the mixture increases.
- Average *M*<sub>r</sub> of mixture decreases.
- (c) Equimolar mixtures of NO and O<sub>2</sub> are allowed to react at two different temperatures. The equation for the reaction is

$$2NO(g) + O_2(g) \implies 2NO_2(g)$$

The colour intensity of the reaction mixture is monitored over a period of time. The graphs below show the variation of the colour intensity with time and at different temperatures.



(i) State the significance of the colour intensity in this reaction.

Colour intensity is proportional to the concentration of  $NO_2$  in the reaction mixture, since  $NO_2$  is the only coloured component in the mixture.

(ii) Using collision theory, explain the difference in the initial slopes of the two graphs.

The initial slope of the graph is proportional to the initial rate of the reaction. The graph at 800 K has greater initial slope compared to that at 750 K, hence its initial

rate is greater. By collision theory, the greater rate at higher temperature is due to more reacting molecules having energy equal to or more than the activation energy. Frequency of effective collision increases hence rate of reaction increases.

(iii) What conclusion can be made about each mixture when the colour intensity reaches a constant value?

The system has reached a state of dynamic equilibrium i.e. rate of forward reaction equals to backward reaction.

(iv) Based on the information given, state whether the formation of NO<sub>2</sub> is endothermic or exothermic.

Forward reaction (or formation of NO<sub>2</sub>) is exothermic.

(v) The kinetics of the reaction between NO and  $O_2$  is investigated and the following results obtained.

Experiment No.	Partial pressure, P <sub>NO</sub> / N m <sup>-2</sup>	Partial pressure, $P_{\Omega 2}$ / N m <sup>-2</sup>	initial rate/ N m <sup>-2</sup> s <sup>-1</sup>
1	0.40	0.60	2.00
2	0.40	0.50	1.67
3	0.50	0.80	4.17

Deduce the order of reaction with respect to NO and  $O_2$ . Hence, write a rate equation for the forward reaction.

Comparing expt 1 and 2, when  $P_{NO}$  is kept constant and  $P_{O2}$  decreased by  $\frac{5}{6}$  times, the initial rate also decreased by  $\frac{5}{6}$  times.  $\Rightarrow$  order of reaction wrt  $P_{O2}$  is one.

Comparing expt 2 and 3,

 $\frac{\text{Initial rate}_2}{\text{Initial rate}_3} = \frac{k(0.50)(P_{\text{NO}})^a}{k(0.80)(P_{\text{NO}})^a}$  $= \frac{k(0.50)(0.40)^a}{k(0.80)(0.50)^a} = \frac{1.67}{4.17}$ 

⇒ a = 2

 $\Rightarrow$  order of reaction wrt  $P_{\rm NO}$  is two.

Rate =  $k(P_{NO})^2(P_{O2})$ 

(vi) Hence, calculate the rate constant and state its units. Using expt 1,

Rate =  $k(P_{NO})^2(P_{O2})$ 2.00 =  $k(0.40)^2(0.60)$ k = **20.8** N<sup>-2</sup> m<sup>4</sup> s<sup>-1</sup>

(vii) Considering your answers in (v), sketch the graph expected for the reaction at a higher pressure, P<sub>1</sub>, and at temperature of 750 K. Label your graph.



No credit is given if graph shows a more gentle slope.

<u>Note</u>: A higher pressure means a larger concentration of gaseous reactants. Since rate is dependent on [reactants] according to the rate law, the rate of the forward reaction will be faster. A higher pressure will also cause equilibrium to shift forward to decrease the total moles of gases in the system. Hence colour intensity at equilibrium will be higher.

[Total: 20]

[10]

**3(a)** Under controlled conditions, alkanes can undergo 'cracking' and reforming to produce alkenes which are more useful.

In the following reactions, alkenes A and B were obtained as shown:

I 
$$CH_3CH_2CH(CH_2CH_3)C(CH_3)_3 \rightarrow C_5H_{10} + (CH_3)_3CH$$
  
A

- II  $CH_3(CH_2)_3CH(CH_2CH_3)CH_3 \rightarrow C_6H_{10} + H_2 + CH_3CH_3$ B
- (i) Based on Reaction I and II, what do you understand by the term 'cracking'?

Cracking is the process by which long–chain alkanes in the higher–boiling fractions of crude oil are broken down into shorter–chain alkanes and alkenes

(ii) State an industrial use for forming alkenes **A** and **B**.

Fuel for petrol engines (since the length of carbon chain for **A** and **B** is  $C_5-C_{12}$ .

(iii) When one mole of alkene **B** reacts with hot acidified KMnO<sub>4</sub>, two moles of carbon dioxide and one mole of 2–methylpropanedioic acid were formed. Explain this reaction and hence draw the structure of **B**.

**B** undergoes strong oxidation with hot acidified  $KMnO_4$ . Since there are 2 mol of carbon dioxide formed, there is a double bond at each end of terminal alkene.  $CH_2$ =CHCH(CH<sub>3</sub>)CH=CH<sub>2</sub>

(v) State and explain the type of stereoisomerism that exists in A. Draw and label the stereoisomers of A.

[7]

cis–trans isomerism as there are 2 different substituents attached to the C of C=C bond.

Structure of A: CH<sub>3</sub>CH=CHCH<sub>2</sub>CH<sub>3</sub>



Correct structure of **A** correct labelling of cis/trans isomer and shape

(b) (i) A student wanted to identify an unknown Group I metal, **R**, using a sample of the Group I carbonate,  $\mathbf{R}_2CO_3$ . She heated a 3.00 g sample of  $\mathbf{R}_2CO_3$  in a boiling tube and the decomposition reaction was as shown:

$$\mathbf{R}_2 CO_3(s) \rightarrow \mathbf{R}_2 O(s) + CO_2(g)$$

The gas evolved was bubbled into a solution of calcium hydroxide. A white precipitate formed was found to have a mass of 2.17 g. Calculate the relative molecular mass of  $\mathbf{R}_2$ CO<sub>3</sub> and hence identify  $\mathbf{R}$ .

 $\begin{array}{l} \text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \\ \text{White ppt formed is CaCO}_3. \\ \text{amount of CaCO}_3 = 2.17 \ / \ 100 = 0.0217 \ \text{mol} \\ = \text{no. of moles of CO}_2 \\ \text{no. of moles of } \mathbf{R}_2\text{CO}_3 = 0.0217 \ \text{mol} \\ \text{M}_r \ \text{of R}_2\text{CO}_3 = 3.00 \ / \ 0.0217 = 138.2 \\ 2(\text{A}_r \ \text{of } \mathbf{R}) + 12.0 + 3(16.0) = 138.2 \\ \text{A}_r \ \text{of } \mathbf{R} = 39.1 \\ \mathbf{R} \ \text{is potassium.} \end{array}$ 

(ii) R<sub>2</sub>O formed in (b)(i) can be dissolved in water to form a strong alkali, ROH. A buffer solution was formed when ROH was added to excess propanoic acid. Explain, with the aid of equations, explain how this buffer solution resists pH change when a small amount of acid or base was added.

When a small amount of acid was added,  $CH_3CH_2COO^- + H^+ \rightarrow CH_3CH_2COOH$  $H^+$  is removed as  $CH_3CH_2COOH$  and hence pH remains almost constant.

When a small amount of base was added,  $CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H_2O$  $OH^-$  is removed as  $CH_3CH_2COO^-$  and  $H_2O$  and hence pH remains almost constant.

(iii) The pH of propanoic acid solution is 2.5. 27.0 cm<sup>3</sup> of 0.2 mol dm<sup>-3</sup> potassium hydroxide was required to fully neutralise 25.0 cm<sup>3</sup> of propanoic acid solution. Write an expression for the acid dissociation constant,  $K_a$ , of propanoic acid and hence calculate a value for  $K_a$  of propanoic acid.

[8]

$$[H^+] = 10^{-2.5} = 3.162 \times 10^{-3} \text{ mol dm}^{-3}$$
  
no. of moles of KOH = 27.0/1000 x 0.2  
= 0.0054 mol  
= no. of moles of propanoic acid

$$[CH_{3}CH_{2}COOH] = 0.0054 / 0.025$$
  
= 0.216 mol dm<sup>-3</sup>  
$$K_{a} = \frac{\left[H^{+}\left[CH_{3}CH_{2}COO^{-}\right]\right]}{\left[CH_{3}CH_{2}COOH\right]}$$
  
=  $\frac{\left(3.162x10^{-3}\right)^{2}}{0.216}$   
= 4.63 x 10<sup>-5</sup> mol dm<sup>-3</sup>  
OR  $K_{a} = \frac{\left[H^{+}\left[CH_{3}CH_{2}COO^{-}\right]\right]}{\left[CH_{3}CH_{2}COOH\right]}$   
=  $\frac{\left(3.162 \times 10^{-3}\right)^{2}}{0.216 - 3.162 \times 10^{-3}}$ 

 $= 4.70 \text{ x } 10^{-5} \text{ mol } \text{dm}^{-3}$ 

(c) (i) Explain fully which compound, propanoic acid or 2–hydroxypropanoic acid, has a lower  $pK_a$  value.

Electron–withdrawing –OH group is present in 2–hydroxypropanoic acid. Hence it will disperse the negative charge of the conjugate base and stabilise the conjugate base to a greater extent. Hence 2–hydroxypropanoic acid is a stronger acid and has a lower  $pK_a$  value.

(ii) Suggest a simple chemical test to distinguish between propanoic acid and 2–hydroxypropanoic acid. Your answers should include the reagents and conditions, observations and balanced equation(s).

Add alkaline aq iodine and warm.

Yellow ppt is seen for 2-hydroxypropanoic acid but no ppt observed for propanoic acid.

 $CH_{3}CH(OH)COOH + 4I_{2} + 7OH^{-} \rightarrow (COO^{-})_{2} + CHI_{3} + 6H_{2}O + 5I^{-}$ 

[5] [Total: 20]