CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

Paper 2 Structured Questions

9647/02
Monday 24th August 2015
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class in the spaces provided above.
Write in dark blue or black pen in the spaces provided, on the Question Paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer all questions.
You are reminded of the need for good English and clear presentation in your answers.

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

ANSWER SCHEME

	For Examiner's Use		
Paper 1		/40	
Paper 2	**Q 1**	/12	
	Q 2	/15	
	Q 3	/15	
	Q 4	/15	
	Q 5	/15	/72
Paper 3	**Q 1**	/20	
	Q 2	/20	
	Q 3	/20	
	Q 4	/20	
	Q 5	/20	/80
Total		/192	

1 Planning (P)

Cream of tartar (potassium hydrogen tartrate, $KHC_4H_4O_6$) is one of the ingredients in baking powder which is used to make cakes rise. Potassium hydrogen tartrate is a weak acid that is not very soluble in water.

$$KHC_4H_4O_6(s) \rightleftharpoons K^+(aq) + HC_4H_4O_6^-(aq)$$

The $HC_4H_4O_6^-(aq)$ ion contains one acidic hydrogen, so the quantity of potassium hydrogen tartrate in solution can be determined by titration with a base.

$$HC_4H_4O_6^-(aq) + OH^-(aq) \rightarrow H_2O(l) + C_4H_4O_6^{2-}(aq)$$

You are to design an experiment to determine the solubility of potassium hydrogen tartrate in two solvent systems: pure water and 0.100 mol dm^{-3} potassium chloride.

In addition to the standard apparatus available in a school laboratory, you are provided with the following materials:

- potassium hydrogen tartrate
- distilled water
- methyl orange indicator
- phenolphthalein indicator
- standard sodium hydroxide solution

(a) Write an expression for the solubility product, K_{sp}, of potassium hydrogen tartrate, stating its units.

$K_{sp} = [K^+]\,[HC_4H_4O_6^-]$ $mol^2\ dm^{-6}$

[1]

(b) When a solution is saturated, the undissolved solid is in equilibrium with its aqueous solution.

$$\mathbf{X}(s) + aq \rightleftharpoons \mathbf{X}(aq)$$

Describe how you would prepare a saturated solution of potassium hydrogen tartrate at room temperature.

- **Dissolve solid $KHC_4H_4O_6$ in water until some solid remains undissolved.**
- **Allow solution to stand for few hours (to establish equilibrium).**
- **Filter to remove undissolved solid. The saturated solution of $KHC_4H_4O_6$ is collected as the filtrate.**

OR

- **Dissolve solid $KHC_4H_4O_6$ in hot water until some solid remains undissolved.**
- **Cool the solution to room temperature to saturate. Excess solid would crystallise out.**
- **Filter to remove excess solid/crystals. The saturated solution of $KHC_4H_4O_6$ is collected as the filtrate.**

[3]

(c) The concentration of a saturated solution of potassium hydrogen tartrate may be determined by titration with standard sodium hydroxide.

(i) Given that, at room temperature, K_{sp} of potassium hydrogen tartrate has a numerical value of 6.27×10^{-4}, suggest an appropriate concentration of the standard sodium hydroxide solution to be prepared. Show your working.

- **for a saturated solution of $KHC_4H_4O_6$, $[K^+][HC_4H_4O_6^-] = K_{sp}$**
- **$\therefore [HC_4H_4O_6^-] = \sqrt{K_{sp}}$ (since $[K^+] = [HC_4H_4O_6^-]$)**

  $= \sqrt{6.27\times10^{-4}} = 0.0250$ mol dm^{-3}
- **To avoid too small a titre value which has high percentage error, or too large a titre value which requires more than one burette full of titrant, [titrant] is chosen such that volume of titrant at end-point is about equal to volume of analyte.**

  Since, $HC_4H_4O_6^- + OH^- \rightarrow C_4H_4O_6^{2-} + H_2O$

  $\therefore$ [NaOH] = $[HC_4H_4O_6^-]$

  = 0.0250 mol dm^{-3}

  $\therefore$ a suitable [NaOH] = 0.0250 mol dm^{-3}

[Accept answers between 0.0200 and 0.0300 mol dm^{-3}]

(ii) Name the indicator used in this titration.

phenolphthalein indicator

[3]

(d) Describe what further experiments you would carry out to determine the solubility of potassium hydrogen tartrate in 0.100 mol dm^{-3} potassium chloride. State clearly the volume of solution used and the expected observation.

- **Prepare a saturated solution of $KHC_4H_4O_6$ in 0.100 mol dm^{-3} KC*l*;**

  i.e. repeat procedure stated in (b) but use 0.100 mol dm^{-3} KC*l* instead of water.
- **Pipette 25.0 cm^3 of the saturated solution of $KHC_4H_4O_6$ prepared above (into a 250 cm^3 conical flask). Add (2-3 drops of) phenolphthalein indicator.**

  Titrate with standard / 0.0250 mol dm^{-3} NaOH (placed in a 50 cm^3 burette) until the solution in the conical flask changed from colourless to pink.

State and explain how the titration result of this further experiment would compare with that of the solution prepared in **(b).**

- **vol of NaOH less than that for saturated solution of $KHC_4H_4O_6$ in water.**
- **Presence of common ion, K^+, lowers/depresses the solubility of $KHC_4H_4O_6$.**

[5]

[Total: 12]

2 Carbon is the fourth most abundant element in the universe by mass after hydrogen, helium and oxygen. It is present in all forms of carbon-based life, and in the human body. This abundance, together with the unique diversity of organic compounds, makes this element the chemical basis of all known life.

(a) (i) Organic compound **P** contains only the elements carbon, hydrogen and oxygen in the following composition by mass: C, 40 %; H, 6.7 %.
Calculate the empirical formula of **P**.

% by mass of O = 100 – 40 – 6.7 = 53.3%
Let mass of compound P be 100 g.

	C	H	O
Mass / g	**40**	**6.7**	**53.3**
Amount / mol	**40 ÷ 12.0 = 3.33**	**6.7 ÷ 1.0 = 6.7**	**53.3 ÷ 16 = 3.33**
Simplest ratio	**1**	**2**	**1**

Hence, the empirical formula of P is CH_2O. ***with working***

(ii) When a 0.102 g sample of compound **P** was vapourised in a suitable apparatus, the vapour occupied 59 cm^3 at 150 °C and 101 kPa.

Calculate the relative molecular mass of compound **P**, and hence determine its molecular formula.

Using ideal gas equation, *pV = nRT*

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

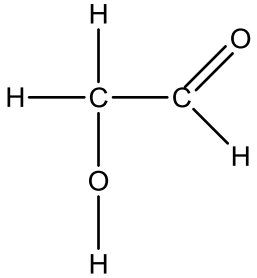
$$\therefore M_r = \frac{mRT}{pV} = \frac{(0.102)\times 8.31\times(150+273)}{(101\times10^3)(59\times10^{-6})}$$ ***correct conversions***

= 60.2 ***correct value to 1 dp; NO units***

Let the molecular formula of P be $C_nH_{2n}O_n$.
Since M_r of $C_nH_{2n}O_n$ = 60.2
n(12.0) + 2n(1.0) + n(16.0) = 60.2
∴ n = 2

Hence, molecular formula of P is $C_2H_4O_2$.

(iii) Compound **P** gives a silver mirror with Tollens' reagent. Draw the displayed formula of compound **P**.



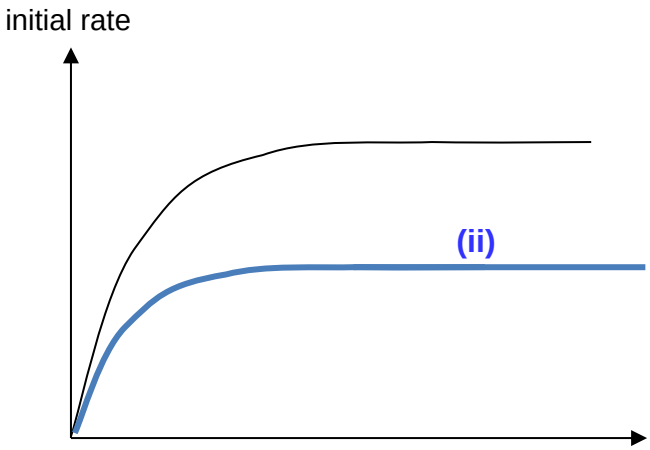
structure & all bonds shown

[5]

(b) Starch is another organic compound consisting of carbon, hydrogen and oxygen. The hydrolysis of starch into simpler sugars can be catalysed by the enzyme amylase. Amylase is present in the saliva of humans and acts as a biological catalyst in the digestion of starch.

(i) A few experiments are carried out with different concentrations of starch solution and the initial rates of hydrolysis in the presence of the enzyme, amylase, are measured.

The graph below shows how the initial rates of the hydrolysis reaction in the presence of amylase vary with the concentrations of starch solution.



max. initial rate is about half that of original graph & graph plateau earlier

Explain the relationship between the concentration of substrate and the initial rate of reaction, making reference to the order of reaction with respect to the substrate concentration.

At low substrate concentration, initial rate increases linearly as substrate/starch concentration increases. The reaction is first order with respect to substrate concentration.

At higher substrate concentrations, initial rate is constant. All the active sites of amylase are in use/saturated. Adding more substrate will not increase rate of reaction. Hence, the reaction is zero order with respect to substrate concentration.

(ii) On the same graph in **(b)(i)**, sketch another graph to show how the initial rates will vary with the concentrations of starch solution if the concentration of amylase is halved. Label this graph as **(ii)**.

[3]

(c) Allotropes are pure forms of the same element that differ in structure. There are several allotropes of carbon such as graphite and diamond.

A mixture of carbon dioxide reacts with hot graphite according to the equation below:

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g) \qquad \Delta H = +170 \text{ kJ mol}^{-1}$$

The mixture was allowed to reach dynamic equilibrium at 817 °C in a 2 dm^3 closed vessel. The amount of CO_2, C and CO at equilibrium is given below.

	CO_2	C	CO
Equilibrium amount / mol	0.1	0.7	1.7

(i) What do you understand by the term *dynamic equilibrium*?

Dynamic equilibrium refers to a reversible reaction in which the rate of forward reaction is equal to the rate of reverse reaction, and there is no change in the concentrations of reactants and products although the reaction is still proceeding.

***Not acceptable*: "*No change in amount*" or "Concentration of reactants and products are the same".**

(ii) Write an expression for the equilibrium constant, K_c, of this reaction, stating the units.

$K_c = \dfrac{[CO]^2}{[CO_2]}$ **mol dm^{-3}** ***both correct expression and units***

(iii) Use the data given and your answer to **(c)(ii)** to calculate a value for K_c of this reaction.

The reaction was carried out in a 2 dm^3 closed vessel.

	$CO_2(g)$ + C(s) $\rightleftharpoons$ 2CO(g)	
Equilibrium conc/ moldm^{-3}	$\frac{0.1}{2}$	$\frac{1.7}{2}$
	= 0.050	**= 0.850**

$$K_c = \frac{[CO]^2}{[CO_2]} = \frac{(0.850)^2}{(0.05)}$$

= 14.5 mol dm^{-3} ***correct value and for dividing eqm conc by 2***

(iv) State, with reasoning, the effect on the position of equilibrium if

(I) the total volume of the system is increased at 817 °C.

Pressure ∝ 1/volume.

If total volume of system is increased, total pressure of the system decreases. By Le Chatelier's Principle, the position of equilibrium shifts to the right [link to pressure] so as to increase the pressure by increasing the number of molecules of gas. *mention of gaseous molecules*

(II) some of the graphite is removed from the equilibrium mixture.

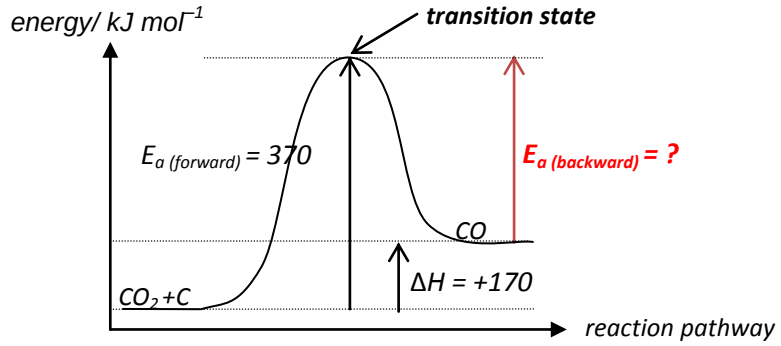
No effect on (or no change in) the position of equilibrium. This is because graphite exists as a solid and its concentration remains unchanged *no effect and for reason*

(v) The activation energy for the forward reaction is 370 kJ mol^{-1}. Calculate the activation energy, in kJ mol^{-1}, for the reverse reaction.

Given ΔH = +170 kJ mol^{-1}, the forward reaction is endothermic.

Hence, activation energy for the reverse reaction = 370 – 170
= 200 kJ mol^{-1}

***Note*:**

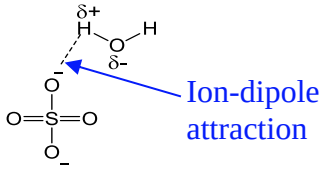


[7]

[Total: 15]

3 **(a)** Manganese sulfate, $MnSO_4$, which is soluble in water, is commonly used to make fungicide. When the sulfate has dissolved, the anions and cations are each surrounded by a number of water molecules.

(i) Draw a simple diagram to show how a water molecule can be attached to a sulfate anion. Label the type of interaction involved.

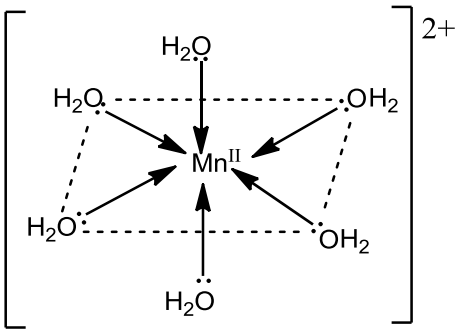


partial charge & charges on SO_4^{2-} & interaction labeled

Note: When an ionic compound dissolves in water, ion-dipole interactions are formed between the cation/anion(ion) and water(dipole).

The aqueous solution of $MnSO_4$ is pale pink in colour due to the presence of complex ion, $[Mn(H_2O)_6]^{2+}$.

(ii) Draw the structure of the complex ion, $[Mn(H_2O)_6]^{2+}$.



lone pairs on H_2O ligands, arrows showing dative bonds, dotted lines showing plane, Roman numeral on Mn^{2+} and square brackets with overall charge on complex

(iii) State the coordination number of the complex ion, $[Mn(H_2O)_6]^{2+}$.

6

(iv) Explain why $[Mn(H_2O)_6]^{2+}(aq)$ is pale pink in colour.

Mn^{2+} [Ar] $3d^5$; Mn^{2+} has incompletely filled (or partially filled) 3d-orbitals. In the presence of ligands, the 3d-orbitals become non-degenerate and split into two groups of slightly different energy levels (d-d* splitting). When electrons from the lower energy level are promoted to the higher energy level (d-d* electronic transition), radiation in the green/blue region of the visible spectrum is absorbed. Light energy not absorbed is thus seen as the colour of the complex, which is pale pink.

[6]

(b) When aqueous ammonia is added gradually to a pale pink solution of $[Mn(H_2O)_6]^{2+}$, an off-white precipitate is observed which rapidly turns brown on contact with air.

(i) Suggest the identity of the off-white precipitate.

$Mn(OH)_2$ or $[Mn(H_2O)_4(OH)_2]$

(ii) Write relevant equations to explain the formation of the off-white precipitate.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$2OH^- + [Mn(H_2O)_6]^{2+} \rightarrow [Mn(H_2O)_4(OH)_2] + 2H_2O$ *OR* $2OH^- + Mn^{2+} \rightarrow Mn(OH)_2$

NH_3 acts as a base and gives OH^- ions in the presence of water. These OH^- ions will then react with $[Mn(H_2O)_6]^{2+}$ to give an off-white precipitate of $[Mn(H_2O)_4(OH)_2]$. [3]

(c) MnO_2 acts as a heterogeneous catalyst in the decomposition of H_2O_2.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g) \qquad \Delta H^\ominus = -196 \text{ kJ mol}^{-1}, \quad \Delta G^\ominus = -224 \text{ kJ mol}^{-1}$$

(i) Use the data to calculate $\Delta S^\ominus$ for this reaction and comment on its sign with respect to the equation for the reaction.

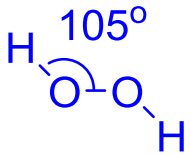
$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$-224 = -196 - (25 + 273)\ \Delta S^\ominus$

$\Delta S^\ominus = +0.0940$ kJ K^{-1} mol^{-1} [with workings]

$\Delta S^\ominus$ is positive because there is an increase in disorder due to the an increase in the number of moles in gaseous particles from 0 to 1.

(ii) Draw the displayed formula to show the bonding in a hydrogen peroxide molecule. Predict and indicate clearly the bond angle in your diagram.



correct structure and correct bond angle (accept 94.8°-105°)

[3]

(d) Alkaline batteries are often used in portable radios and electric torches. In an alkaline battery, the reaction at the cathode involves the reduction of MnO_2 to Mn_2O_3 while the reaction at the anode is as follows:

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

(i) State the oxidation number of manganese in Mn_2O_3.

+3

(ii) Write a half-equation for the reaction that occurs at the cathode.

$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$

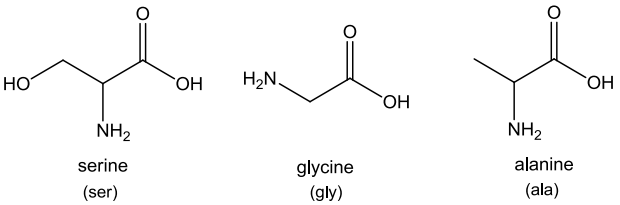
(iii) Hence, construct the equation for the overall reaction.

$2MnO_2 + Zn \rightarrow Mn_2O_3 + ZnO$

[3]

[Total: 15]

4 **(a)** Silk emitted by the silkworm consists mainly of the insoluble protein fibroin surrounded by a layer of glue-like substance. The protein secondary structure of fibroin consists mostly of layers of anti-parallel beta-pleated sheets and its primary structure is a recurrent 6-amino acid residue sequence consisting of only serine, glycine and alanine.



Partial hydrolysis of fibroin results in the following fragments.

ala-gly-ala , ser-gly-ala, gly-ser

(i) Using the same 3-letter abbreviations as above, write out the recurrent 6-amino acid residue sequence of fibroin based on the information provided.

gly-ser-gly-ala-gly-ala

(ii) From your answer in **(a)(i)** and the proportion of individual amino acids in the protein structure, suggest why close packing is possible in the polypeptide chain.

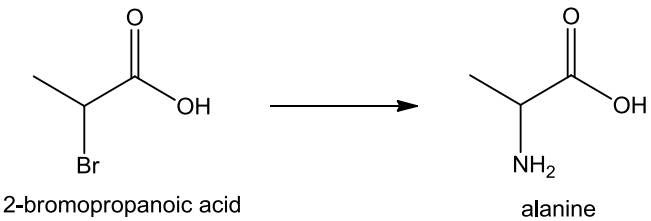
Close packing is possible due to the high proportion (50%) of glycine where glycine's R group is only a hydrogen atom and so is not as sterically constrained.

(iii) With reference to the secondary structure of fibroin, describe what is meant by denaturation, clearly making reference to any bonding or interaction involved.

Denaturation is the process that alters the hydrogen bonding between the C=O group of one polypeptide strand and the N-H group of the adjacent polypeptide strand in the beta-pleated sheets of the secondary structure of fibroin.

[3]

(b) Alanine is a non-essential amino acid and can be manufactured by the human body. Alanine can also be chemically synthesised from 2-bromopropanoic acid.



(i) State the reagents required to synthesise alanine from 2-bromopropanoic acid.

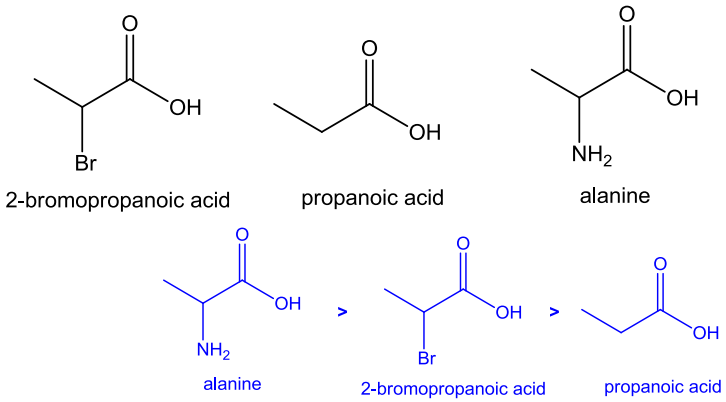
Reagents: ..**ammonia**.....

(ii) Identify the inorganic by-product from the reaction shown above.

By-product: .**HBr or NH_4Br**.....

The pK_a associated with 2-bromopropanoic acid is 3.00. The two pK_a associated with alanine are 2.35 and 9.69 and its isoelectric point is 6.01.

(iii) Arrange the following compounds in order of decreasing acidity. Explain your answer in terms of their structural properties.



Order of decreasing acidity: .....

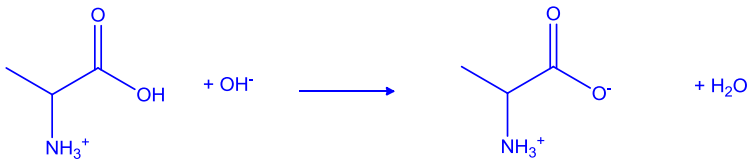
Explanation:

Alanine is the strongest acid as it contains the most electronegative / electron-withdrawing amino group increasing the polarisation of O–H bond, and so weakening the O–H bond, thus making it easier for the acid to lose the H^+. 2-bromopropanoic acid is the second strongest acid as it contains slightly less electronegative Br atom compared to the amino group and propanoic acid is least acidic due to the absence of any electronegative / electron-withdrawing substituent group present.

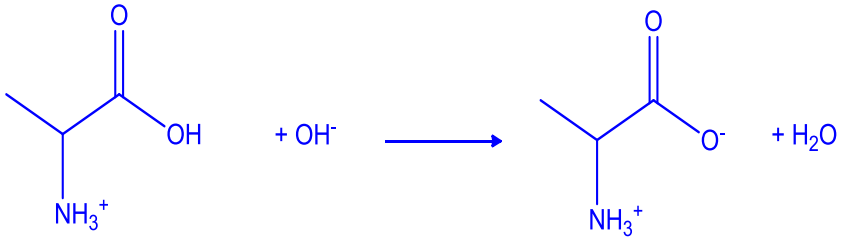
Credit was given to candidates who were able to clearly explain why 2-bromopropanoic acid is a stronger acid than propanoic acid, even if the order between alanine and 2-bromopropanoic acid was wrongly given.

***Also accept answers mentioning stability of conjugate ion* and formation of intramolecular H-bonding within the conjugate base ion of alanine.**

(iv) Write an equation to show how alanine can act as a buffer when a small amount of $OH^-(aq)$ is added at pH 2.35.



(v) Calculate the pH of the resulting solution when 7.5 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10.0 cm^3 of 0.100 mol dm^{-3} of the protonated form of alanine.

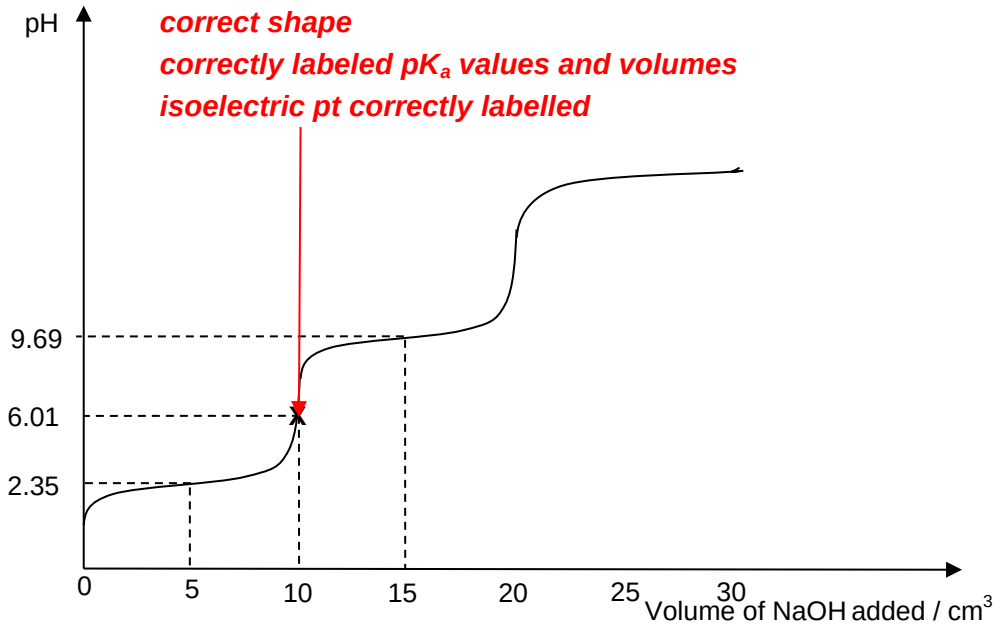


Start:	**$10 \times \frac{0.10}{1000}$ = 0.001 mol (excess reagent)**	**$7.5 \times \frac{0.10}{1000}$ = 0.00075 mol (limiting reagent)**	**0**
end:	**0.00025 mol**	**0 mol**	**0.00075 mol**

Hence, resulting solution contains a weak acid and its conjugate base (i.e. forms an acidic buffer)

$\therefore$ pH = p*K*a + lg $\frac{[salt]}{[acid]}$ = 2.35 + lg $\frac{0.00075}{0.00025}$ = 2.83

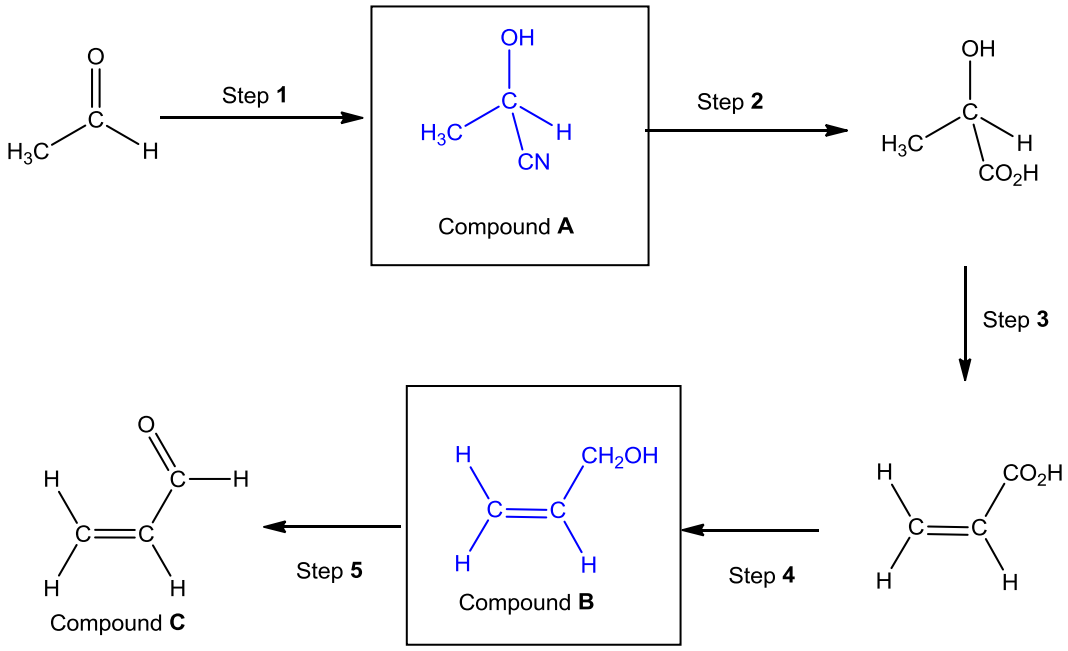
(vi) Sketch the pH-volume curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} of the protonated form of alanine. Show clearly on your curve where the two pK_a values occur and the isoelectric point.



[12]

[Total: 15]

5 **(a)** Compound **C** may be synthesised from ethanal as follows:



State the reagents and conditions required for Steps **3** – **5** and give the structures of the intermediate organic compounds **A** and **B** in the boxes provided.

Reagents and conditions

Step **3** **(excess) concentrated H_2SO_4, 170˚C** .....

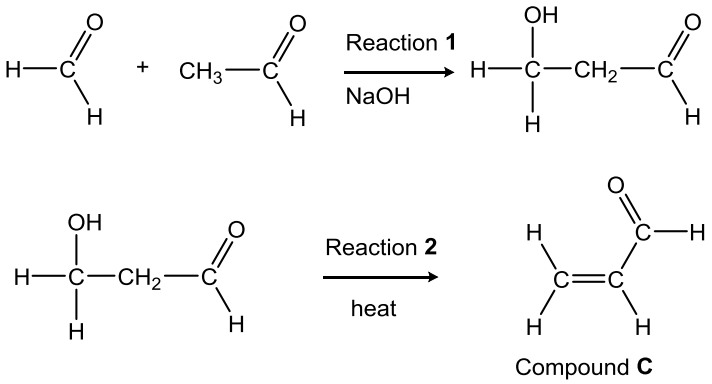
Step **4** **$LiAlH_4$ in dry ether** .....

Step **5** **$K_2Cr_2O_7$, dilute H_2SO_4, heat with distillation** .....

[5]

(b) Aldol condensation reaction is a useful method for making new carbon–carbon bonds in organic chemistry. In the presence of a strong base, two carbonyl compounds can undergo the aldol condensation reaction.

The same product, compound **C**, from part **(a)** can also be obtained from ethanal and methanal via the aldol condensation. The reaction proceeds as follows.

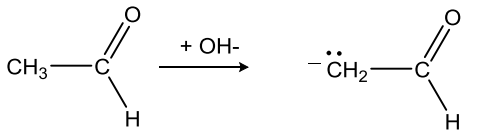


(i) Identify the type of reaction occurring in Reaction **2**.

Elimination (also accept dehydration)

Reaction **1** of the aldol condensation consists of three steps. The first step involves the removal of hydrogen from the alpha carbon of one carbonyl compound to form an enolate ion. The alpha carbon is the carbon adjacent to the carbonyl group.

Step **I**:



(ii) State the type of reaction occurring in Step **I**.

Acid-base reaction or neutralisation

[Turn over

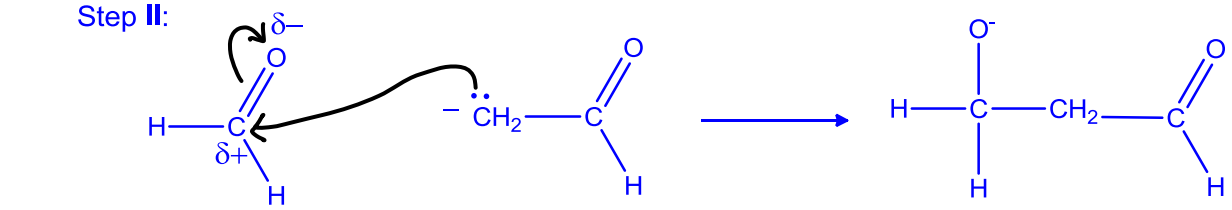
(iii) Steps **II** and **III** are as follows:

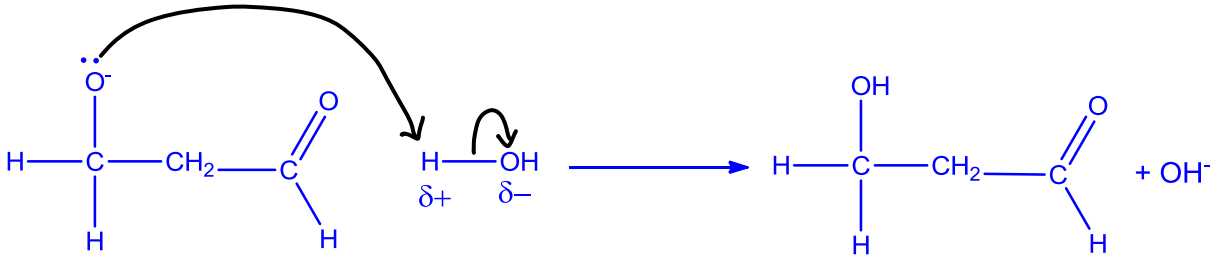
Step **II**: nucleophilic attack on methanal to form an alkoxide ion

Step **III**: protonation of the alkoxide ion by water

Using the above information, suggest the mechanism for Steps **II** and **III**, showing all charges and using curly arrows to show the movement of electron pairs.

Step **II**:



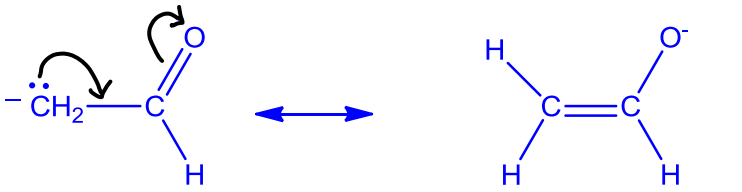


all 2 correct arrows and partial charges indicated (Step II)

all 2 correct arrows and partial charges indicated (Step III)

correct alkoxide given

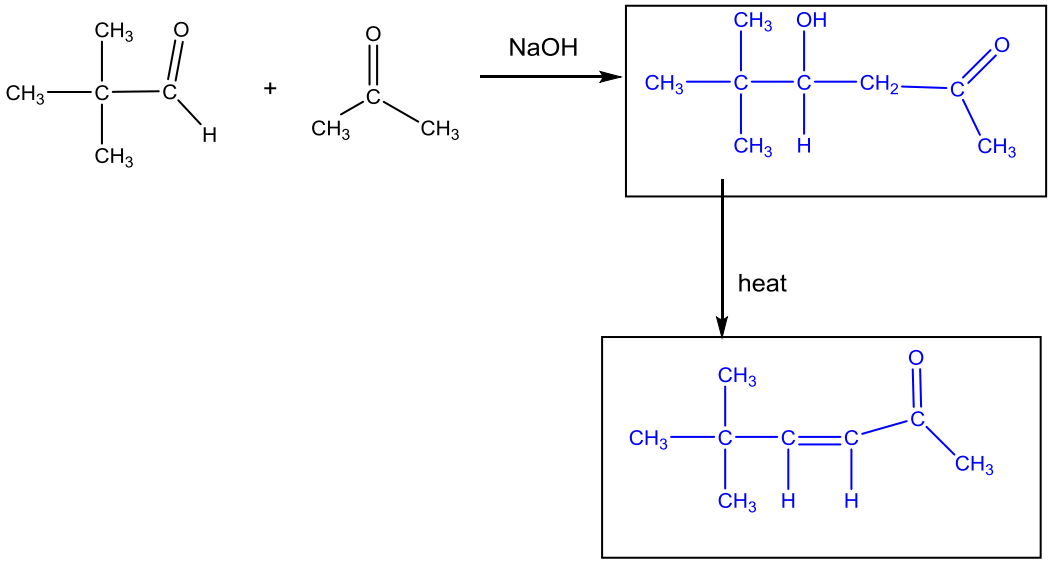
(iv) Given that the negative charge on the enolate ion can be delocalised, draw another possible structure in which the enolate ion can exist as.



enolate ion

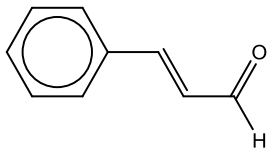
correct structure

(v) Complete the reaction sequence for the following aldol condensation, by giving the structural formulae for the compounds involved in the boxes provided.



[8]

(c) Cinnamaldehyde is an organic compound that gives cinnamon its flavour and odour. Cinnamaldehyde can also be synthesised in the laboratory via the aldol condensation reaction.

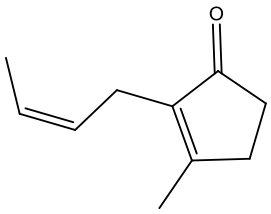


cinnamaldehyde

(i) State the type of stereoisomerism that cinnamaldehyde can exhibit.

geometrical or cis-trans isomerism

(ii) Jasmone is the active ingredient in jasmine which is used in the perfume industry. The structure of jasmone is shown below.



State the reagents and conditions for a simple chemical test that could be used to distinguish between cinnamaldehyde and jasmone.

Add Tollens' reagent and heat

or Fehling's and heat

or $K_2Cr_2O_7$, dilute H_2SO_4 and heat

[2]

[Total: 15]