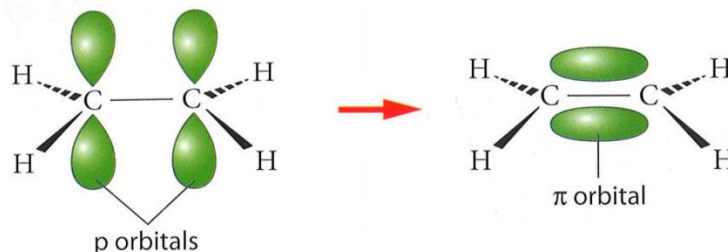


2014 H1 Preliminary Examination Solution

Paper 2: Section A

1 Benzene is a commonly used chemical, especially in the production of plastics and fibres.

(a) With the aid of a diagram, explain the formation of a π bond, using ethene as an example.



A **side-on overlap** of the p-orbitals causes the formation of a π bond.

[2]

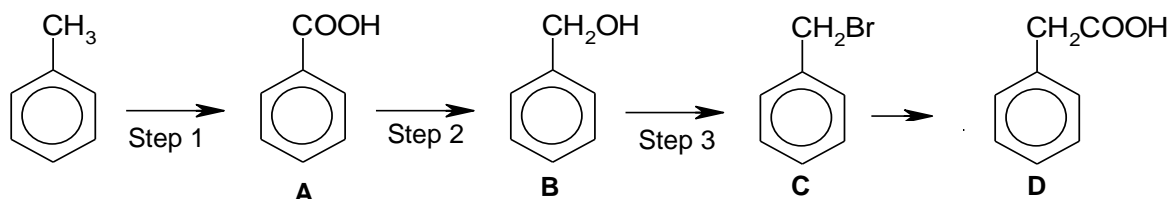
(b) Compare the relative reactivity of benzene and phenylethene towards addition reactions. Explain your answer.

Benzene does not undergo addition reaction as this destroys the **resonance stability** of

benzene. Phenylethene undergoes addition reaction readily.

[2]

- (c) The following diagram shows some reactions of methylbenzene.



- (i) State the type of reaction for Step 2.

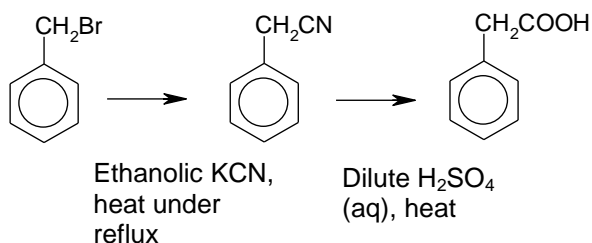
Reduction

- (ii) There is *another* route to obtain **C** from methylbenzene in *one* step. Give the reagent and conditions for this method and explain why this method **not** preferred.

Reagent and conditions: $\text{Br}_2(l)$, UV light

Explanation: Free radical substitution is uncontrollable and multi-substituted products may be obtained.

- (iii) Propose a 2- step synthetic pathway for the conversion of **C** to **D**. Give the reagents and conditions for all steps, and the structure of any intermediates.

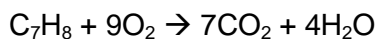


- (iv) Suggest how the acidity of **A** might compare to that of **D**. Give reasons for your answers.

The negative charge on carboxylate anion, COO^- of **A** is more dispersed than **B** as it is able to delocalise into the benzene ring as compared to **B**, where the $-\text{CH}_2-$ group between the benzene ring and the COO^- prevents the delocalisation. Hence the carboxylate anion of **A** is more stable than **B**.

[8]

- (d) 5 cm^3 (density = 0.87 g cm^{-3}) of methylbenzene was completely burnt in excess oxygen. Calculate the volume of carbon dioxide produced at s.t.p.



Mass of methylbenzene = $5 \times 0.87 = 4.35 \text{ g}$

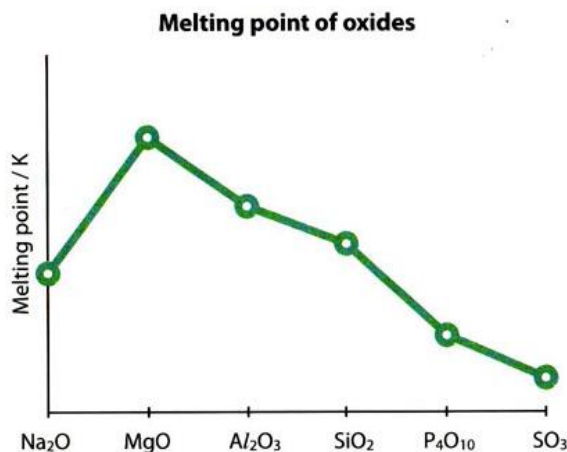
Number of moles of methylbenzene = $4.35 / [(12.0 \times 7) + 8.0] = 0.0473 \text{ mol}$

Number of moles of carbon dioxide = $0.0473 \text{ mol} \times 7 = 0.331 \text{ mol}$

Volume of carbon dioxide = $0.331 \times 22.4 = 7.41 \text{ dm}^3$

[2]
[Total:10]

- 2 (a) Complete the sketch for elements of the third period to show how the melting points of the oxides vary.



[1]

- (b) Explain, in terms of bonding and structure, the difference in melting point between:

Na₂O and MgO

Na₂O, MgO have giant **ionic structures**. The melting point of MgO is higher as Mg²⁺ has a **smaller ionic radii and higher charge** than Na⁺. Thus its lattice energy $\frac{q^+q^-}{r_+ + r_-}$ is larger.
More energy is needed to overcome the stronger electrostatic forces of attraction.

SiO₂ and SO₃

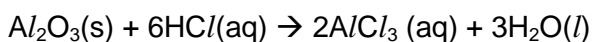
SiO₂ has a **giant molecular structure** held by **strong covalent bonds** between the Si and atoms. SO₃ has a **simple molecular structure** with **weak van der Waals' attraction between molecules**. **Less energy** is needed to overcome the weaker forces, thus SO₃ has a lower melting point.

[4]

- (c) The labels on 2 bottles containing aluminium oxide and silicon dioxide have been torn off. Describe a test which you could carry out in order to distinguish between these 2 oxides. Include the reagents, observations and equations for any reaction that occurs.

Add HCl(aq) to a sample of both compounds.

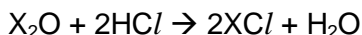
Aluminium oxide dissolves, while silicon oxide does not.



[3]

- (d) A 0.150 g sample of a Group I oxide was dissolved in water. It was then titrated with 0.200 mol dm⁻³ hydrochloric acid. 24.20 cm³ of hydrochloric acid was needed for complete reaction. Calculate the M_r of the oxide.

Let the formula of the metal oxide be X₂O



Number of moles of HCl = (24.20/1000) × 0.200 = 4.84 × 10⁻³ mol

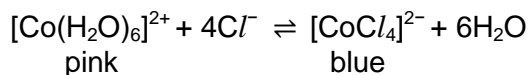
Number of moles of X₂O = (4.84 × 10⁻³)/2 = 2.42 × 10⁻³ mol

M_r of oxide = 0.1500 / (2.42 × 10⁻³) = 62.0

[2]

[Total:10]

- 3 The following equation shows an equilibrium reaction for aqueous cobalt(II) chloride solution.



- (a) The reaction above can serve as a humidity sensor. State the colour when the sensor is moist.

Pink

[1]

- (b) When a solution of aqueous cobalt(II) chloride was placed in ice water, the solution changed from pink to blue. State the enthalpy change for the reaction and explain your answer.

The **forward reaction is favored** as the solution changed from pink to blue.

By Le Chatelier's principle, when temperature is lowered, system tries to increase the

temperature by favoring the **exothermic** reaction. Thus ΔH is exothermic.

[2]

- (c) Adding a few drops of hydrochloric acid causes the pink aqueous cobalt(II) chloride solution to turn blue. Explain the observations.

When HCl is added, $[\text{Cl}^-]$ is increased. Hence system responds to **decrease the $[\text{Cl}^-]$** by

shifting the equilibrium to the **right**. More $[\text{CoCl}_4]^{2-}$ is formed, thus solution turns blue.

[1]

[Total:5]

- 4 Household bleaches contain the active ingredient sodium hypochlorite. The concentration of hypochlorite ion, ClO^- in bleaches can be determined by performing a series of redox reactions.

Under acidic conditions, ClO^- can oxidise iodide ions to iodine. The amount of iodine liberated can be found by titration with a standard solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

- (a) (i) Define the term *redox* reactions.

A redox reaction is one where **oxidation and reduction** occurs **simultaneously**.

- (ii) State the oxidation state of chlorine in ClO^- .

+1

[2]

- (b) A student performed the following steps to determine the concentration of ClO^- in Brand X's bleach solution.

Step 1: Brand X bleach solution was first diluted by adding 20 cm^3 of Brand X bleach solution to 100 cm^3 of distilled water.

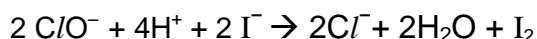
Step 2: An excess of potassium iodide was added to 25.0 cm^3 of the diluted bleach solution, and acidified with dilute sulfuric acid.

Step 3: The mixture obtained from **Step 2** was titrated against $0.100 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3$. When the solution turned pale yellow, starch was added, and the student continued titration until the reaction was complete. 23.90 cm^3 of $\text{Na}_2\text{S}_2\text{O}_3$ was required for complete reaction.

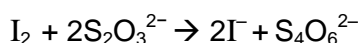
- (i) State the observations upon completion of the reaction in **Step 3**.

Solution changes from dark blue to colourless.

- (ii) Construct balanced equations between:
 ClO^- and I^- to form Cl^- and I_2 (in acidic medium)



I_2 and $\text{S}_2\text{O}_3^{2-}$ to form I^- and $\text{S}_4\text{O}_6^{2-}$



- (iii) Calculate the number of moles of iodine liberated by the reaction between ClO^- and I^- .

Number of moles of sodium thiosulfate

$$= \frac{23.90}{1000} \times 0.100 = 2.39 \times 0.100 = 2.39 \times 10^{-3} \text{ mol}$$

$$\text{Number of moles of iodine} = \frac{1}{2} \times 2.39 \times 10^{-3} = 1.20 \times 10^{-3} \text{ mol}$$

- (iv)

Hence, determine the concentration of ClO^- in Brand X bleach.

Number of moles of ClO^-

$$= 1.20 \times 10^{-3} \times 2 = 2.39 \times 10^{-3} \text{ mol (in } 25 \text{ cm}^3 \text{ of diluted bleach)}$$

Number of moles of ClO^- in 100 cm^3 diluted bleach

$$= 2.39 \times 10^{-3} \times (100/25) = 9.56 \times 10^{-3} \text{ mol}$$

Concentration of ClO^- in original bleach solution

$$= (9.56 \times 10^{-3}) \div 20/1000 = 0.478 \text{ mol dm}^{-3}$$

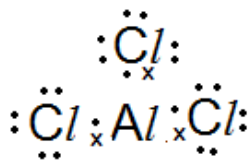
[8]

[Total:10]

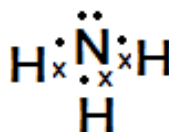
Section B

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

- 5 (a) Draw the 'dot-and-cross' diagrams to show the bonding in aluminium chloride and ammonia, stating their shapes. Use the diagrams to help to explain why the bond angle in aluminium chloride is 120° and in ammonia is 107° .



Shape: **trigonal planar**



Shape: **trigonal pyramidal**

There are three regions of electron densities/ three electron pairs around aluminium in aluminium chloride are directed in a **trigonal planar manner to minimise electrostatic repulsion**. Since all the three electron pairs are bond pairs, it is trigonal planar in shape and the bond angle is 120° .

There are four regions of electron densities/ four electron pairs around nitrogen in ammonia, directed in a **tetrahedral manner to minimise electrostatic repulsion**. There are three bond pairs and one lone pair. **Lone pair-bond pair repulsion is greater than bond-pair bond-pair repulsion**, the bond pairs in ammonia are forced closer together, resulting in a bond angle of 107° .

[7]

- (b) Ammonia is manufactured industrially in the Haber Process. Describe this process including an equation for the reaction, the condition used, and the reasons that these particular conditions are chosen.

The Haber Process which is used to manufacture ammonia.



Conditions: **250 atm**, **450°C**, Finely divided **iron catalyst**

The forward reaction is accompanied by a **decrease** in number of gaseous moles. According to Le Chatelier's Principle, the equilibrium shifts to the right when the pressure exerted on the system is **high**.

The forward reaction is **exothermic**. According to Le Chatelier's Principle, the equilibrium shifts to the right when the temperature is **low**.

Although higher pressures and lower temperature will increase the yield of ammonia, reaction vessels that can withstand high pressures incur high cost and rate of reaction at low temperatures is too slow. Hence, the selected pressure and temperature is a compromise between yield and cost.

Or The reactor is coated with finely divided iron to speed up the reaction. The use of the catalyst **does not** increase the yield of ammonia.

[5]

(c) The student prepared two solutions.

- Solution **A** was made by mixing 25 cm³ of 0.10 mol dm⁻³ of dilute hydrochloric acid with 50 cm³ of 0.10 mol dm⁻³ of ammonia. Solution **A** is a buffer solution.
- Solution **B** was made by mixing 50 cm³ of 0.10 mol dm⁻³ of dilute hydrochloric acid with 25 cm³ of 0.10 mol dm⁻³ of ammonia. Solution **B** is **not** a buffer solution.

(i) Explain why solution **B** is **not** a buffer solution.

For solution B, 25 cm³ of 0.10 mol dm⁻³ of ammonia reacts with 25 cm³ of 0.10 mol dm⁻³ of dilute hydrochloric acid, forming 25 cm³ of ammonium chloride (conjugate acid of weak base, ammonia). However, all the ammonia has fully reacted. It is not a buffer solution.

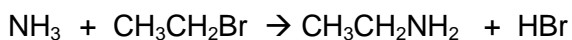
(ii) Write two balanced equations to show how solution **A** is able to maintain pH when small amounts of acid and base are added to it.

When a small amount of H⁺ is added: $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$

When a small amount of OH⁻ is added: $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$ **note: “→”**

[3]

(d) Ammonia reacts with bromoethane. Give an equation for this reaction stating any conditions required. State the type of reaction involved.



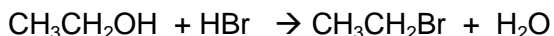
Condition: ethanol, heat in sealed tube

Type of reaction: substitution

[3]

- (e) In the laboratory, bromoethane is prepared by addition of HBr to ethene.

There is an alternative reaction to prepare bromoethane in the lab using a suitable alcohol. Suggest the reagents and conditions for this reaction and write a balanced equation for it.



Or



[2]
[Total:20]

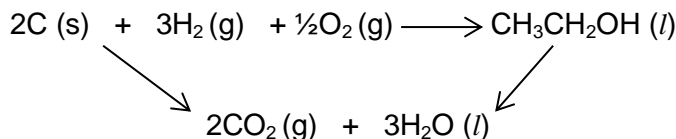
- 6 (a) (i) In a flame calorimetry experiment, when 1.00 g of ethanol was combusted, it heated 150 cm³ of water from 25°C to 70°C. Find the enthalpy change of combustion of ethanol. The density of water is 1 gcm⁻³. Assume that the specific heat capacity of water to be 4.2 Jg⁻¹K⁻¹.

$$\begin{aligned}\text{Heat evolved, } q &= mc\Delta T = 150 \times 4.2 \times 45 \\ &= 28350 \text{ J} = 28.35 \text{ kJ}\end{aligned}$$

$$\text{Amount of ethanol} = \frac{1}{46} = 0.02174 \text{ mol}$$

$$\begin{aligned}\Delta H_c &= -\frac{q}{\text{number of moles of fuel}} \\ &= -\frac{28.35}{0.02174} = \mathbf{-1304 \text{ kJ mol}^{-1} \text{ or } -1300 \text{ kJ mol}^{-1}}\end{aligned}$$

- (ii) Using the following data and the energy cycle below, calculate another value for the standard enthalpy change of combustion of ethanol.



$$\begin{aligned}\Delta H_c^\theta \text{ carbon} &= -394 \text{ kJmol}^{-1} \\ \Delta H_c^\theta \text{ hydrogen} &= -286 \text{ kJmol}^{-1} \\ \Delta H_f^\theta \text{ ethanol} &= -277.7 \text{ kJmol}^{-1}\end{aligned}$$

By Hess' law,

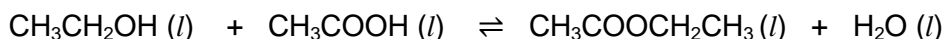
$$\begin{aligned}\Delta H_c \text{ ethanol} &= \Delta H_c \text{ carbon} - \Delta H_f \text{ ethanol} \\ &= 2(-394) + 3(-286) - (-277.7) \\ &= \mathbf{-1368.3 \text{ kJ mol}^{-1} = -1370 \text{ kJ mol}^{-1}}\end{aligned}$$

- (iii) Suggest a reason for the difference in the answer from **a(i)** and **a(ii)**.

Heat is loss to surrounding in a(i), resulting is a less exothermic enthalpy change of combustion calculated.

[6]

- (b) Ethanol and ethanoic acid react together in the presence of sulfuric acid. The following equilibria is established, in which ester, ethyl ethanoate, is present.



- (i) Write an expression for the equilibrium constant, K_c , for the reaction between ethanol and ethanoic acid shown above.

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]}$$

- (ii) 2.00 moles of ethanoic acid and 3.00 moles of ethanol were mixed in a closed vessel. At equilibrium, 1.50 moles of ethyl ethanoate are present. The total volume of the reaction mixture is 1 dm³. Calculate a value for K_c .

	$\text{CH}_3\text{CH}_2\text{OH}(l) + \text{CH}_3\text{COOH}(l) \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l)$			
Initial mol	3	2	0	0
Change	-1.5	-1.5	+1.5	+1.5
Eqm mol	1.5	0.5	1.5	1.5
Eqm []	1.5	0.5	1.5	1.5

$K_c = 3$ (no units)

- (c) Compound **G** has the following molecular formula $\text{C}_5\text{H}_9\text{O}_2\text{Cl}$. Upon adding sodium carbonate to **G**, effervescence was observed. [4]

Compound **G** produced a yellow precipitate with hot aqueous alkaline iodine.

Compound **G** does not decolourise hot acidified KMnO_4 .

Compound **G** reacts with hot aqueous sodium hydroxide to give **J**.

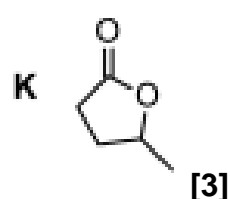
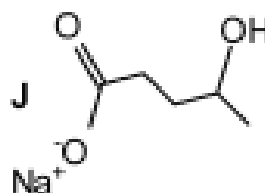
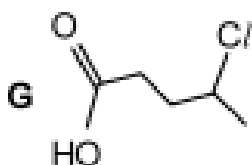
Upon acidification, **J** forms compound **K**, $\text{C}_5\text{H}_8\text{O}_2$ in the presence of a small amount of hot concentrated sulfuric acid.

Compound **K**, $\text{C}_5\text{H}_8\text{O}_2$ has the following characteristics.

- It does not exhibit geometric isomerism.
- It does not decolourise aqueous bromine.

Identify and suggest the structures for **G**, **J**, and **K**. Show how you deduced these structures by explaining the reactions that are occurring.

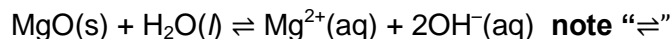
Information	Deduction
Compound G $C_5H_9O_2Cl$. Upon adding sodium carbonate to G , effervescence was observed.	<ul style="list-style-type: none"> Compound G contains $-COOH$ group. From the molecular formula, $C-Cl$ bond is present.
Compound G produced a yellow precipitate with hot aqueous alkaline iodine.	<ul style="list-style-type: none"> Halogenoalkane/$C-Cl$ bond in compound G undergoes substitution with the alkaline (OH^-) to form alcohol $R-OH$/ $C-OH$. $R-OH$ further undergoes oxidation to give a positive tri-iodo methane test. Presence of $CH_3CH(OH)-$ structure.
Compound G does not decolourise hot acidified $KMnO_4$.	<ul style="list-style-type: none"> Compound G does not undergo oxidation.
Compound G reacts with hot aqueous sodium hydroxide to give J .	<ul style="list-style-type: none"> The $COOH$ group in G reacts undergoes acid-base reaction/neutralisation with $NaOH$ to form a salt $COO-Na^+$. The Halogenoalkane/$C-Cl$ in G reacts with hot $NaOH$ via substitution reaction to form $R-OH$.
Upon acidification, J forms compound K , $C_5H_8O_2$ in the presence of a small amount of hot concentrated sulfuric acid.	<ul style="list-style-type: none"> Condensation reaction occurs.
Compound K , $C_5H_8O_2$ has the following characteristics. <ul style="list-style-type: none"> It does not exhibit geometric isomerism. It does not decolourise aqueous bromine. 	<ul style="list-style-type: none"> K does not have alkene functional group. K is an ester.
	<ul style="list-style-type: none"> Max [7] marks



[10]
[Total:20]

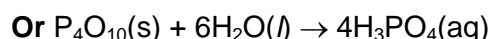
- 7 (a) Using the oxides of magnesium, silicon and phosphorus as examples, describe the reactions of the oxides of elements in the third period of the Periodic Table with water. Include balanced equations for any reactions.

MgO is **partially soluble** in water due to highly exothermic lattice energy.



SiO₂ is insoluble in water as it is a giant covalent compound.

P₄O₆ and P₄O₁₀ are **soluble** in water to form acids.



[4]

- (b) The reaction between **X** and **Y** is monitored by finding the time taken for **X**, a coloured reactant to decolourise. Water is added to the reaction mixture to keep the volume of the reaction mixture for experiment 1, 2 and 3 constant at 60 cm³.



The following results are obtained:

Experiment	Volume of X added/cm ³	Volume of Y added/cm ³	Volume of H ₂ O added/cm ³	Relative rate of reaction
1	10	20	30	1
2	15	40	5	6
3	20	20	20	2
4	60	40	20	r

- (i) Explain why is there a need to keep the total volume of the reaction mixture constant.

When the total volume is constant, the initial concentration of each reactant in the reaction mixture is directly proportional to its volume used.

- (ii) Deduce, showing your working, the orders of reaction with respect to **X** and **Y**. Hence, write the overall rate equation for this reaction.

Comparing experiment 1 and 3, where volume(concentration) of Y is constant, when volume(concentration) of X doubles, the relative reate of reaction doubles. Hence order of reaction with respect to X is 1.

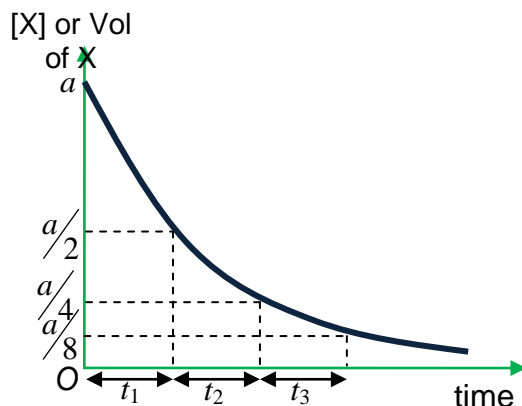
Comparing experiment 1 and 2, when concentration of x increased by 1.5 times, the relative rate increased from 1 to 1.5. When concentration of Y doubles, the relative rate (6/1.5) increased by 4 times. Hence order of reaction with respect to Y is 2.

$$\text{Rate} = k[\text{X}][\text{Y}]^2$$

- (iii) Deduce the value of r in experiment 4.

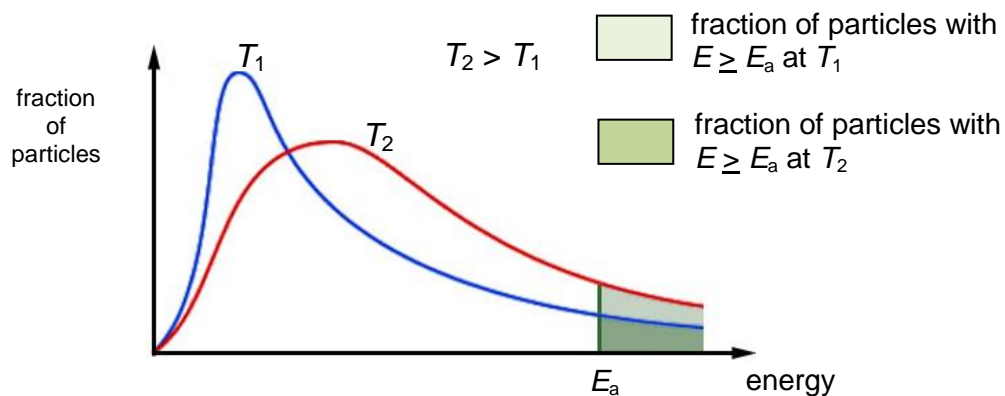
24

- (iv) Sketch a concentration time-graph for X in this reaction.



Graph

- (v) Sketch a Boltzmann distribution curve for the reactants and use it to explain the effect of increasing temperature on the rate of reaction.



As seen from the graph, When temperature increases, a **greater fraction (or legend)** of the particles will have energy **greater than the activation energy** required for reaction. Hence, there will be a **higher no of successful collisions**. Rate increased.

[10]

- (c) The presence of C=C bonds in unsaturated fat make the fat turn rancid easily as it is more prone to breakdown. In food production, liquid unsaturated fats such as vegetable oils are hydrogenated to produce saturated fats such as margarine, which have higher melting point than unsaturated fat.

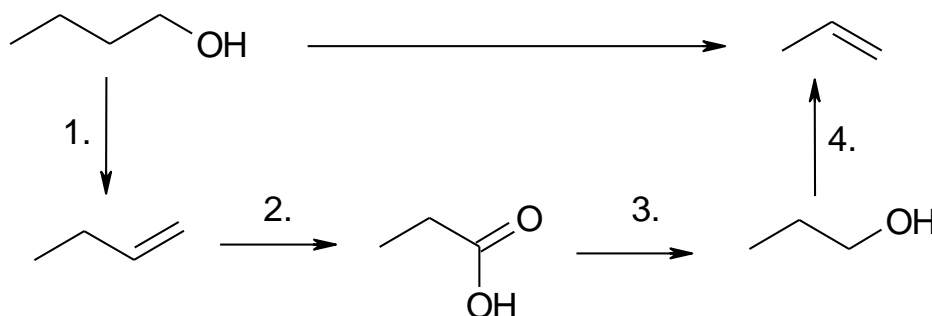
- (i) Why is the melting point of saturated fat higher than unsaturated fat?

Presence of multiple C=C in unsaturated fats make the structure more **spherical** hence **smaller surface area**, for molecular interaction as compared to saturated fats, which has a bigger surface area. Hence **stronger van der Waals'** attraction exists between saturated fat molecules and it has a higher melting point.

Or

Saturated fats has **more electrons**, electron cloud is more polarisable hence **stronger van der Waals'** attraction exists between saturated fat molecules and it has a higher melting point.

- (ii) Suggest a synthetic route for the formation of prop-1-ene from butan-1-ol.



1. conc H_2SO_4 , 170°C
2. dilute H_2SO_4 , KMnO_4 , Heat
3. LiAlH_4 in dry ether
4. conc H_2SO_4 , 170°C

[6]

[Total:20]

~ END OF PAPER ~