



Preliminary Examinations Higher 1

CANDIDATE
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CHEMISTRY

8872/02

Paper 2

29 August 2014

Candidates answer Section A on the Question Paper.

2 hours

Additional Materials: Answer Paper
Data Booklet
Graph Paper

READ THESE INSTRUCTIONS FIRST

Write your Civics Group number and candidate name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A

Answer **all** questions.

Section B

Answer **two** questions on separate answer paper.

At the end of the examination, Section A and Section B will be handed in separately.
The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use		
Paper 1	/30	
Paper 2	A1	/14
	A2	/8
	A3	/8
	A4	/10
	B	/20
	B	/20
Total	/110	

Section A

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

For
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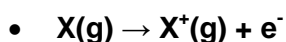
1 This question is about Period 3 elements and compounds.

(a) The values below indicate the successive ionisation energies of a Period 3 element, X.

1000 2260 3390 4540 7000 8500 27110 31720

(i) Define first ionisation energy with the aid of an equation.

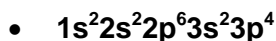
- **First ionisation energy is the minimum energy required to completely remove one mole of electrons from one mole of gaseous atoms in the ground state.**



(ii) Deduce the identity of X. Hence, write its electronic configuration.

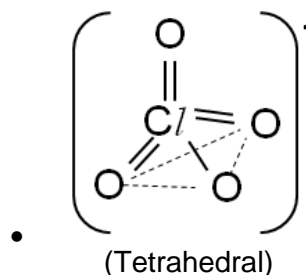
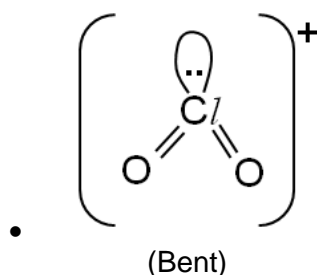
- **There is a large increase between the 6th and 7th ionisation energies. Hence, X contains 6 valence electrons. The 7th electron comes from an inner quantum shell.**

- **X is sulfur.**



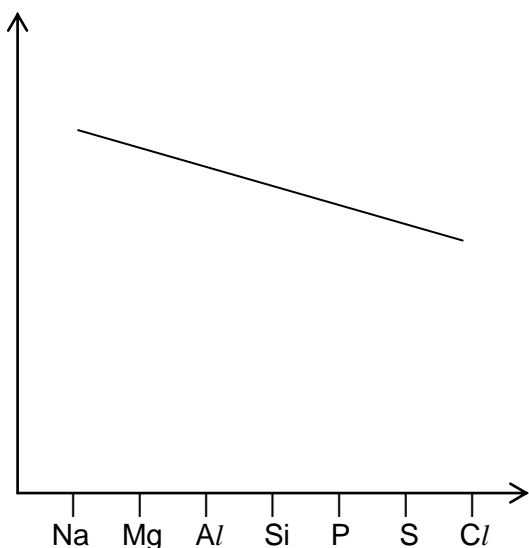
[5]

(b) Chlorine can react with oxygen to give Cl_2O_6 in the gaseous state. In the liquid or solid form, the compound ionises into ClO_2^+ and ClO_4^- . Draw the shape of the ions.

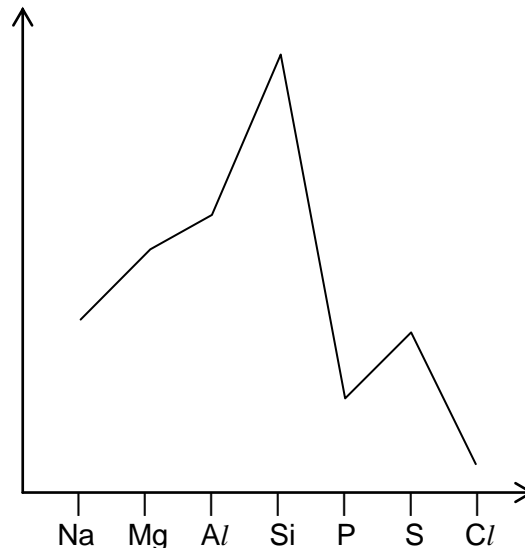


[2]

- (c) Graphs **A** and **B** show the trends of two physical properties of Period 3 elements.



Graph A



Graph B

- (i) Identify the physical properties represented by the two graphs.
- Graph A: Atomic radius
 - Graph B: Melting point
- (ii) In terms of structure and bonding, explain the trend shown by the last 4 elements in Graph B.
- Silicon has a giant molecular structure. Melting involves breaking of numerous strong covalent bonds between the atoms. Large amount of energy is needed.
 - Phosphorus, sulfur and chlorine have simple molecular structures and melting involves breaking of weak van der Waals forces between the molecules.
 - The size of electron clouds and ease of polarisation of $S_8 > P_4 > Cl_2$. Hence the strength of van der Waals' forces and melting point of $S_8 > P_4 > Cl_2$.

[5]

- (d) A solid mixture contains two oxides of Period 3 elements. To separate the oxides, water was added to the mixture, followed by filtration. Effervescence was observed when sodium carbonate was added to the filtrate. The residue does not react with dilute acid and dilute alkali.

(i) Identify the 2 oxides present in the mixture.

- P_4O_6 / P_4O_{10} and SiO_2

(ii) Hence, write an equation for the reaction of one of the oxides with water.

- $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$
OR $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_3$

[2]

[Total: 14]

2 (a) Explain what is meant by the term *bond energy*.

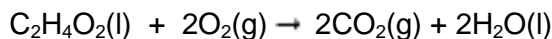
- It refers to the average energy required to break one mole of covalent bonds in the gaseous state into constituent gaseous atoms.



(Note: Equation is for reference only)

[1]

(b) Ethanoic acid burns as shown by the following equation:



- (i) Using bond energies given in the *Data Booklet*, calculate the enthalpy change for the combustion of ethanoic acid as shown in the equation above.

- | | |
|---|---|
| { | <p>Bonds broken: 1 C–C, 3 C–H, 1 C=O, 1 C–O, 1 O–H, 2 O=O</p> <p>Energy absorbed = 350 + 3(410) + 740 + 360 + 460 + 2(496) = 4132 kJ mol⁻¹</p> |
| { | <p>Bonds formed: 4 C=O, 4 O–H</p> <p>Energy released = 4(740) + 4(460) = 4800 kJ mol⁻¹</p> |

- $\Delta H^\circ_c = 4132 - 4800$
 $= -668 \text{ kJ mol}^{-1}$

- (ii) Given that the experimentally determined value for enthalpy change of combustion of ethanoic acid is -209 kJ mol^{-1} , explain the discrepancy between this value and your answer in (b)(i).

• The discrepancy arise because bond energies in the Data Booklet are only average values.

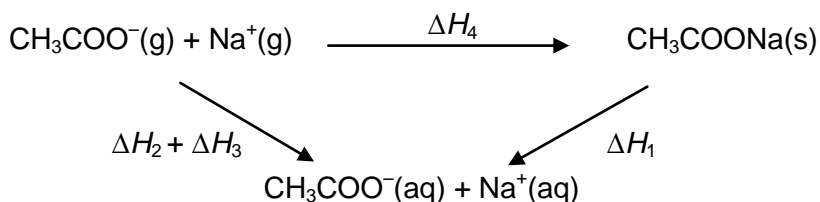
OR

ΔH_c° values assume that all the substances are in standard states, where ethanoic acid and water are liquids at 298K. Bond energies however assume that the bonds in ethanoic acid and water are in the gaseous phase.

[3]

- (c) Sodium ethanoate is an inexpensive chemical that is widely used as a pickling agent. Pickling is a food preservation method that enhances flavor. Essentially, food to be pickled, such as a cucumber, is soaked in a solution of sodium ethanoate that imparts a salty and sour taste.

The enthalpy change for the solution of sodium ethanoate in water, ΔH_1 can be determined by using the energy cycle given below.



$$\Delta H_2 = -375 \text{ kJ mol}^{-1}$$

$$\Delta H_3 = -405 \text{ kJ mol}^{-1}$$

$$\Delta H_4 = -763 \text{ kJ mol}^{-1}$$

- (i) Name the enthalpy change that is represented by ΔH_4 .

• ΔH_4 represents lattice energy.

- (ii) With reference to the energy cycle and the data given above, calculate ΔH_1 .

$$\begin{aligned}
 \bullet \text{ By Hess' Law, } \Delta H_1 &= -\Delta H_4 + \Delta H_2 + \Delta H_3 \\
 &= -(-763) + (-375) + (-405) \\
 &= -17 \text{ kJ mol}^{-1}
 \end{aligned}$$

- (iii) Would you expect the magnitude of the lattice energy of CH_3COOK to be larger or smaller compared to that of CH_3COONa ? Explain your answer.

• The magnitude of the lattice energy of CH_3COOK would be smaller compared to that of CH_3COONa .

• Lattice energy $\propto \left| \frac{q^+ q^-}{r^+ + r^-} \right|$. The K^+ ion has a bigger cationic radius compared to Na^+ ion, hence it has a lower charge density.

[4]

[Total: 8]

- 3 We usually think of iron occurring in compounds in the +2 or +3 oxidation states. However, other oxidation states of iron are possible; for example, potassium ferrate (VI), K_2FeO_4 , contains iron in the +6 oxidation state. The FeO_4^{2-} ion is a stronger oxidizing agent than the MnO_4^- ion. In acidic conditions, FeO_4^{2-} ions are reduced to Fe^{3+} ions. Hence K_2FeO_4 can be used in analytical chemistry for redox titrations.

In one such titration, 25.0 cm^3 of 6.60 g dm^{-3} aqueous ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, is found to require 37.5 cm^3 of potassium ferrate (VI) solution for complete reaction.

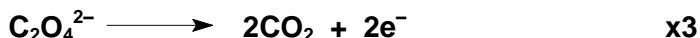
Relevant half-equations for this reaction are given below.



- (a) Using oxidation numbers, explain why this reaction is described as a redox reaction. [2]

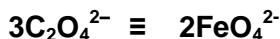
Oxidation number of C in $\text{C}_2\text{O}_4^{2-}$ increases from +3 to +4 in CO_2 while Fe in FeO_4^{2-} decreases from +6 to +3 in Fe^{3+} .

- (b) Use the two half-equations given above to construct a balanced ionic equation for the reaction between $\text{C}_2\text{O}_4^{2-}$ and FeO_4^{2-} ions, showing your working clearly. [2]



- (c) Hence calculate the concentration, in g dm^{-3} , of potassium ferrate (VI) used in the titration.

[A_r of Fe = 55.8]



$$\bullet \quad n(\text{C}_2\text{O}_4^{2-}) \text{ in } 25.0 \text{ cm}^3 = \frac{25}{1000} \times \frac{6.60}{2(1.0) + 2(12.0) + 4(16.0)} = 1.833 \times 10^{-3} \text{ mol}$$

$$\bullet \quad n\text{FeO}_4^{2-} \text{ in } 37.5 \text{ cm}^3 = \frac{2}{3} \times 1.833 \times 10^{-3} = 1.22 \times 10^{-3} \text{ mol}$$

$$\bullet \quad [\text{K}_2\text{FeO}_4] = \frac{1000}{37.5} \times 1.22 \times 10^{-3} = 0.0325 \text{ mol dm}^{-3}$$

$$\bullet \quad [\text{K}_2\text{FeO}_4] \text{ in } \text{g dm}^{-3} = 0.0325 \times [2(39.1) + 55.8 + 4(16.0)] = \underline{6.45 \text{ g dm}^{-3}}$$

[4]

[Total: 8]

- 4 Carboxylic acids may be decarboxylated to form alkanes by an electrochemical reaction known as the *Kolbe* electrolysis reaction.

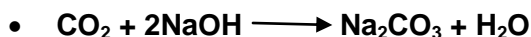
When a mixture of the sodium salts of two different mono-carboxylic acids is electrolysed, a mixture of alkanes is produced.



Electrolysing a mixture of the sodium salts of the two mono-carboxylic acids **A** and **butanoic acid** produced three alkanes **hexane**, **B** and **C**, which could be separated by fractional distillation.

- (a) 1.00 g sample of **B** was burned in an excess of oxygen. The gases that were produced were first passed through a U-tube containing phosphorus pentoxide (to absorb the water vapour) and then bubbled through concentrated NaOH (to absorb carbon dioxide). The phosphorus pentoxide U-tube increased in mass by 3.10 g, and the NaOH(aq) bottle increased in mass by 6.06 g.

- (i) Write an equation for the reaction of carbon dioxide with concentrated NaOH.



- (ii) Use these data to calculate the H : C ratio in alkane **B**, and hence suggest its molecular formula.

$$\text{Number of moles of H}_2\text{O} = 3.10 / 18 = 0.172 \text{ mol}$$

$$\text{Number of moles of CO}_2 = 6.06 / 44 = 0.138 \text{ mol}$$

$$\bullet \text{ Hydrogen to carbon ratio} = (2 \times 0.172) / 0.138 = 2.50$$

$$\text{i.e. } 2.5\text{H} : 1\text{C} \Rightarrow 10\text{H} : 4\text{C}$$

$$\bullet \text{ Empirical formula} = \text{C}_2\text{H}_5, \text{ Molecular formula} = \text{C}_4\text{H}_{10}$$

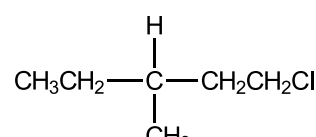
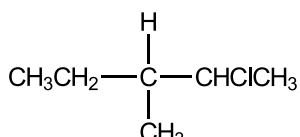
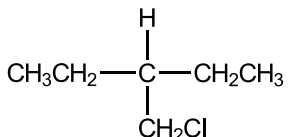
- (iii) Use your results in (ii) to deduce possible structures for the alkane **C** and the acid **A**.

- Since **B** is a symmetrical **C**₄ alkane, acid **A** must be **C**₂**H**₅**CO**₂**H** or propanoic acid
- **C** is **R-R'** → **C**₅**H**₁₀ or pentane.

[5]

- (b) In another separate experiment, a new alkane **D**, **C**₆**H**₁₄, was produced. Alkane **D** undergoes free radical substitution to form compound **E**, 3-chloro-3-methylpentane.

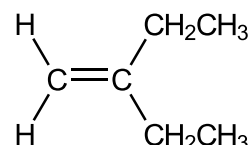
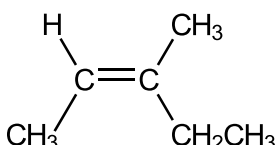
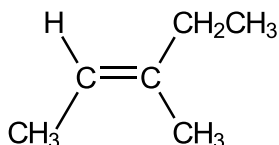
- (i) Compound **E** has 3 other positional isomers. Give the structural formulae of all 3 isomers.



[2 correct structures – 1m; 3 correct – 2m]

- (ii) Compound **E** undergoes elimination of **HCl** to form a mixture of isomeric alkenes.

Suggest the structural formulae of the isomeric alkenes formed. State the type of stereoisomerism (if any) shown.

[1m: cis trans isomers and 1m: 3rd isomer]

- Geometric or cis trans isomerism

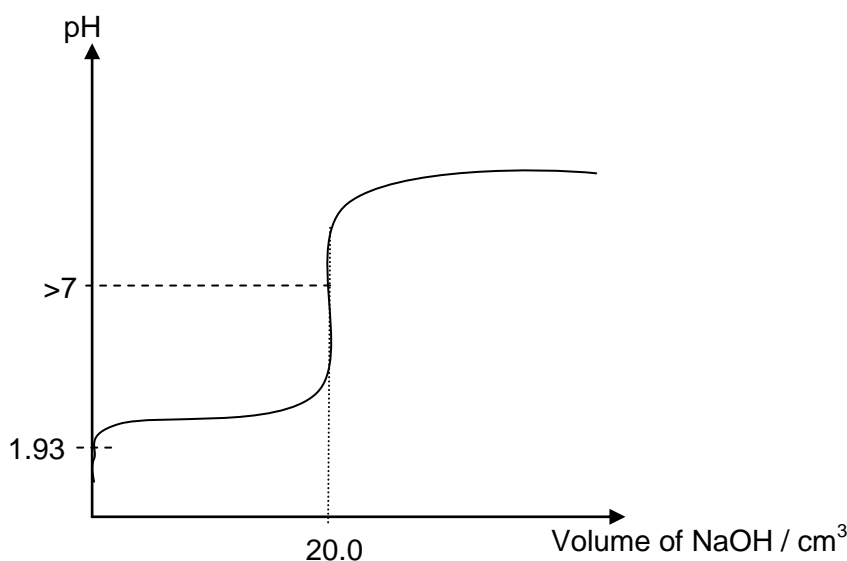
[5]

[Total: 10]

Section B

Answer **two** of the three questions in this section on separate paper.

- 5 Chloroethanoic acid, ClCH_2COOH is a chemical intermediate for production of various pharmaceuticals and insecticides.
- (a) In an experiment, 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ of ClCH_2COOH is titrated with aqueous sodium hydroxide. The titration curve for the above titration was given below.



- (i) Using the pH value of the chloroethanoic acid shown in the graph, calculate the concentration of the hydrogen ions in the solution of chloroethanoic acid.
- pH of chloroethanoic acid = 1.93**
- $[\text{H}^+] = 10^{-1.93} = 0.0117 \text{ mol dm}^{-3}$
- (ii) Explain the difference between the concentration of $[\text{H}^+]$ calculated in (i) and the concentration of chloroethanoic acid.
- **$[\text{H}^+]$ is lower than [acid] as chloroethanoic acid is a weak acid that has undergone partial dissociation.**
- (iii) The above titration experiment was done using screened methyl orange as an indicator. Deduce if screened methyl orange is a suitable indicator. If not, suggest an alternative suitable indicator for the above titration.
- **Screened methyl orange is not a suitable indicator because the pH at equivalence point of titration is >7 and it does not coincide with the working pH range of the indicator.**
 - **Suitable indicator: Phenolphthalein or thymol blue**

[4]

- (b) A student titrated 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ of NaOH(aq) in the conical flask against $0.100 \text{ mol dm}^{-3}$ of $\text{C/CH}_2\text{COOH}$ in the burette. Deduce if an acidic buffer is formed when 10.0 cm^3 of $\text{C/CH}_2\text{COOH}$ is added into the solution.

- **No. An acidic buffer is not formed.**

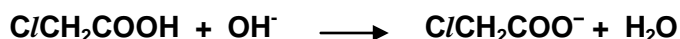
Because when 10.0 cm^3 of $\text{C/CH}_2\text{COOH}$ is added, the species present in the mixture is $\text{C/CH}_2\text{COO}^-$ and excess NaOH (not neutralized).

[1]

- (c) A buffer solution was formed when 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ of $\text{C/CH}_2\text{COOH}$ and 10 cm^3 of $0.100 \text{ mol dm}^{-3}$ of $\text{C/CH}_2\text{COONa}$ are mixed.

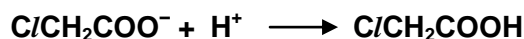
- (i) Explain, using relevant equations, how the above buffer controls pH when a small amount of HCl (aq) or NaOH (aq) is added.

Adding small amount of OH^- ,



OH^- is neutralised by the weak acid. Negligible change in pH

Adding small amount of H^+



The salt, $\text{C/CH}_2\text{COO}^-$, reacts with H^+ to form $\text{C/CH}_2\text{COOH}$. Negligible changes in pH as H^+ ions are removed.

- *1m – balanced equations*
- *1m – explanation*

- (ii) The pH of an acidic buffer solution can be calculated by the given equation,

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

where K_a is the acid dissociation constant of the organic acid.

Calculate the concentration of the salt and the acid in the acidic buffer solution formed and hence, calculate the pH of the buffer solution. [Given that K_a of $\text{C/CH}_2\text{COOH}$ is $1.40 \times 10^{-3} \text{ mol dm}^{-3}$.]

- **$\text{pK}_a = -\lg (1.4 \times 10^{-3}) = 2.85$**
- $\left\{ \begin{array}{l} [\text{salt}] = [(10/1000) \times 0.1] \div (30/1000) = 0.0333 \text{ mol dm}^{-3} \\ [\text{acid}] = [(20/1000) \times 0.1] \div (30/1000) = 0.0666 \text{ mol dm}^{-3} \end{array} \right.$
- **$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$**
- **$\text{pH} = 2.85 + \lg (0.0333/0.0666) = 2.55 \text{ (3sf)}$**

[5]

(d) The K_a values of three carboxylic acids are listed in the table below:

Acid	$K_a / \text{mol dm}^{-3}$
CH_3COOH	1.8×10^{-5}
ClCH_2COOH	1.4×10^{-3}
Cl_2CHCOOH	5.5×10^{-2}

Describe and explain the acid strength illustrated by these values.

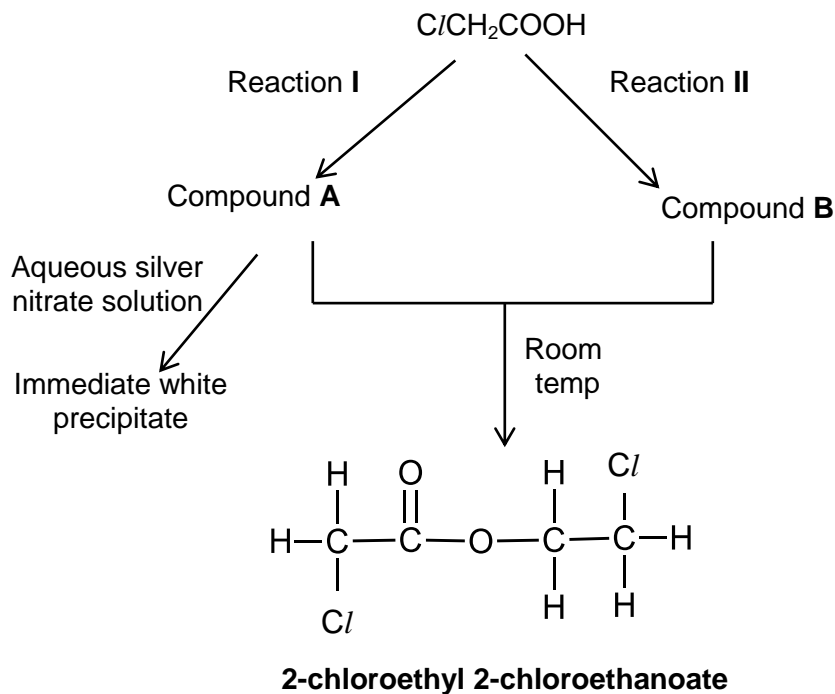
- The larger the K_a value, the stronger the acid.

Acid strength: $\text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{CO}_2\text{H}$

- Cl atom, being electronegative, is electron withdrawing, leading to greater dispersal of negative charge on $\text{ClCH}_2\text{COO}^-$. Thus, $\text{ClCH}_2\text{COO}^-$ is more stable than CH_3COO^- , making ClCH_2COOH a stronger acid than $\text{CH}_3\text{CO}_2\text{H}$.
- Two Cl atoms present in $\text{Cl}_2\text{CHCOO}^-$ disperse the negative charge to a greater extent, thus $\text{Cl}_2\text{CHCOO}^-$ is more stable than $\text{ClCH}_2\text{COO}^-$. Cl_2CHCOOH is a stronger acid than ClCH_2COOH .

[3]

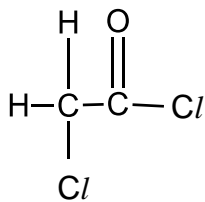
(e) 2-chloroethyl 2-chloroethanoate can be synthesised through the synthetic route shown below, starting with only chloroethanoic acid.



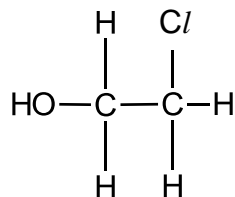
(i) State the reagents and conditions for reaction I and II.

- **Reaction I: $\text{PCl}_5(\text{s})$, cold**
- **Reaction II: LiAlH_4 , in dry ether as solvent, room temperature**

(ii) Draw the structural formula for Compound A and B.



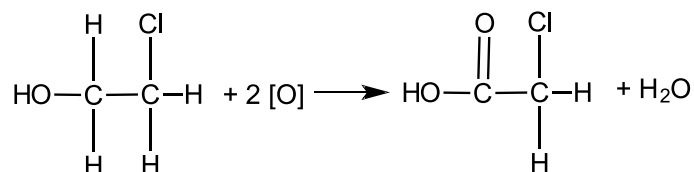
• **Compound A:**



• **Compound B:**

(iii) Describe a simple chemical test that you could use to distinguish between chloroethanoic acid and compound B. You are to include reagents and conditions, observations and balanced equation(s) in your answer.

- **Acidified KMnO_4 , heat**
- **Observation: Chloroethanoic acid - Purple KMnO_4 remained purple. Compound B - Purple KMnO_4 decolourizes to form a colourless solution.**
- **Balanced equation:**



Alternative answers:

1. Aqueous $\text{Na}_2\text{CO}_3 \rightarrow$ effervescence observed for chloroethanoic acid but no effervescence observed for Compound B



[7]

[Total: 20]

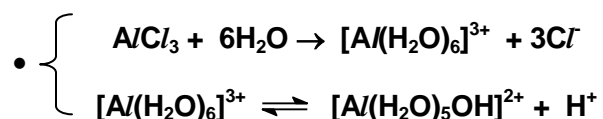
- 6 (a) The chlorides MgCl_2 , AlCl_3 and SiCl_4 differ considerably in their structures and chemical properties. The chlorides become more acidic across the period.

Illustrate this statement by describing the reactions, if any, of the chlorides with water, suggesting the pH of the resulting solutions and writing equations where appropriate.

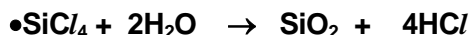
[6]

• MgCl_2 has a giant ionic structure with strong ionic bonds. Hydrated magnesium ion undergoes very slight hydrolysis due to the higher charge density of Mg^{2+} . It forms a slightly acidic solution with pH = 6.5.

• AlCl_3 has a simple molecular structure with weak van der Waals forces' of attraction between its molecules. When a large amount of water is added, both hydration and hydrolysis occur. Al^{3+} has a high charge density and draws electrons away from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule. It forms an acidic solution with pH = 3.

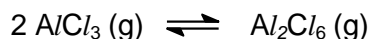


• SiCl_4 has a simple molecular structure with weak van der Waals forces' of attraction between its molecules. It undergoes hydrolysis because of the energetically accessible vacant 3d orbitals in Si available for dative bonding with water molecules. It forms an acidic solution with pH = 2.



• all pH correct

- (b) Solid aluminium chloride sublimes at 180°C . In the vapour phase, an equilibrium is established between aluminium chloride and its dimer.



- (i) Write an expression for the equilibrium constant, K_c , for this reaction and state its units.

$$\bullet K_c = [\text{Al}_2\text{Cl}_6]/[\text{AlCl}_3]^2$$

$$\bullet \text{Units: mol}^{-1} \text{ dm}^3$$

Given that the value of K_c for the reaction is 4.0, calculate the equilibrium amount of Al_2Cl_6 when 0.4 moles of $AlCl_3$ is allowed to reach equilibrium in a 1 dm^3 vessel at high temperatures.

- Let x be the no of moles of Al_2Cl_6 at equilibrium.

$$2\text{ AlCl}_3(\text{g}) \rightleftharpoons \text{Al}_2\text{Cl}_6(\text{g})$$

Initial amount / mol	0.4	0
Change in amount / mol	- 2x	+ x
Final amount / mol	0.4 - 2x	+ x

$$K_c = x/(0.4-2x)^2 = 4.0$$

$$x = 0.115 \text{ mol (reject } x = 0.347)$$

- Equilibrium amount of $Al_2Cl_6 = 0.115 \text{ mol}$

- (ii) Describe and explain how will the composition of the equilibrium mixture be affected by

- I increasing the pressure,
- II increasing the temperature of the system.

[7]

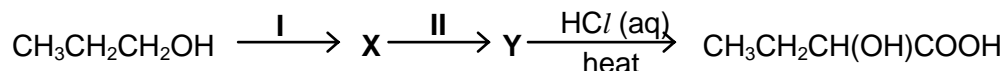
I increasing the pressure

- Since the forward reaction is accompanied by a decrease in the number of moles of gaseous molecules, by Le Chatelier's Principle, an increase in pressure will shift the position of equilibrium to the right so as to reduce the total pressure, forming more Al_2Cl_6 and lesser $AlCl_3$.

II increasing the temperature of the system

- Since the forward reaction involves bond formation, it is an exothermic reaction. • By Le Chatelier's Principle, when temperature increase, system will counteract the change by shifting the position of the equilibrium to the left so as to absorb heat, decreasing the amount of Al_2Cl_6 and forming more $AlCl_3$.

- (c) 2-hydroxybutanoic acid can be produced from propan-1-ol according to the reaction scheme given below:



- (i) Identify compounds X and Y.

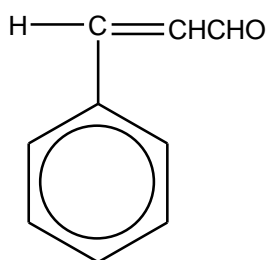
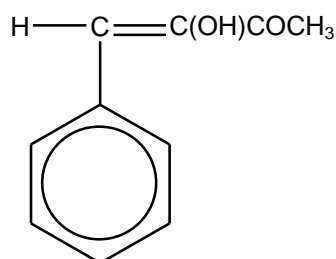
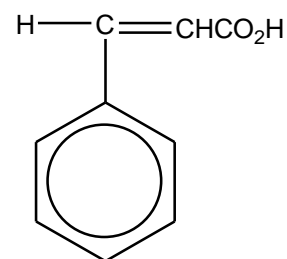
- X: $\text{CH}_3\text{CH}_2\text{CHO}$
- Y: $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$

(ii) State the reagents and conditions for steps I and II.

- I: acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (aq), warm with immediate distillation
- II: HCN (aq) in the presence of an alkali at $10 - 20^\circ\text{C}$
(or HCN (aq) and a small amount of KCN at $10 - 20^\circ\text{C}$)

[4]

(d) For each of the compounds **A** to **C**, state the reagents and conditions for a positive test which would distinguish it from the other two and describe the observations that would be seen.

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

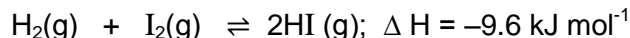
[3]

Compound	Test and Observation
A	<ul style="list-style-type: none"> • Test: Add Tollens' reagent to the 3 samples separately and warm Observation: Silver mirror formed Alternative test: Fehling's reagent, warm Observation: Reddish brown ppt formed
B	<ul style="list-style-type: none"> • Test: Add alkaline aqueous iodine to the 3 samples separately and warm Observation: Yellow ppt of CHI_3 was observed
C	<ul style="list-style-type: none"> • Test: Add Na_2CO_3 to the 3 samples separately at r.t.p Observation: Effervescence of CO_2 was observed.

Note: There must be a positive test for the compound that is to be identified.

[Total: 20]

- 7 (a) Halogens react with hydrogen to form hydrogen halides. The reaction below has an activation energy of $+173.2 \text{ kJ mol}^{-1}$.



The reaction is first *order* with respect to each of the reactant concentrations.

- (i) What do you understand by the term *order of reaction*?
- **Order of reaction is the power to which the concentration of reactant is raised in the experimentally determined rate equation.**
- (ii) Calculate the activation energy of the reverse reaction.
- **Activation energy of the reverse reaction, $E_a = 173.2 + 9.6 = +182.8 \text{ kJ mol}^{-1}$**
- (iii) State and explain how the rate constants k_f and k_b for the forward and reverse reactions and the equilibrium constant K_c for the reaction in (a) would change, if at all,
- with an increase in temperature,
 - in the presence of a catalyst.
 - **With an increase in temperature, frequency of collision & fraction of molecules with energy $\geq E_a$ increase. Hence, frequency of effective collision increases, k_f and k_b would increase.**
 - **By Le Chatelier's principle, increase temperature would shift the equilibrium position to the left hand side as backward reaction is an endothermic reaction and absorbs heat. Hence, K_c decreases.**

Note: (k_f and k_b is proportional to the fraction of molecules that possess the required energy \geq activation energy, E_a .)

- **Catalyst provides an alternative pathway with lower E_a' . As $E_a' < E_a$, fraction of molecules with energy $\geq E_a'$ increases. Hence, k_f and k_b would increase.**

[OR alternative answer for marker: Rate = $k[\text{reactant}]^n$, in the presence of catalyst, rate of reaction increases but concentration of reactant is kept constant, hence, k_f and k_b would increase.]

- **Since rate of forward reaction and the rate of backward (OR k_f and k_b) would increase to the same extent, K_c is not affected**

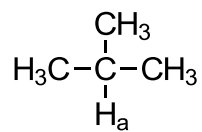
[6]

- (b) Halogens also react with alkanes to form halogenoalkanes. However, synthesis of halogenoalkanes from alkanes is seldom employed as a synthetic route as there could be several isomeric products being formed in the reaction.
- (i) 2-methylpropane reacts with bromine gas under ultraviolet light to form a mixture of two isomeric products, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane.

The relative rates of abstraction of H atoms are given in the table below:

Type of H atoms	Relative rate of abstraction
Primary	1
Secondary	4
Tertiary	6

Predict and explain the ratio of the two isomeric products, taking into account the relative rates of abstraction.



9 possible (primary) hydrogens (H) can be substituted to form 1-bromo-2-methylpropane

1 possible (tertiary) hydrogens (H_a) can be substituted to form 2-bromo-2-methylpropane.

Assuming equal probability of abstraction,

•Ratio of 1-bromo-2-methylpropane : 2-bromo-2methylpropane = 9:1

However since a tertiary H is abstracted 6 times faster than a primary H

•Ratio of 1-bromo-2-methylpropane : 2-bromo-2methylpropane

$$= 9 \times 1:1 \times 6$$

$$= 9:6$$

$$= 3:2$$

[working :1 mark; answer:1 mark]

- (ii) Describe suitable chemical test(s) to distinguish the two isomeric molecules, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane.

- Add NaOH(aq) to both unknowns, heat (to form alcohols) followed by KMnO_4 , NaOH(aq), heat.
- Observation for 1-bromo-2-methylpropane: Purple KMnO_4 decolourised, Brown ppt of MnO_2 formed as 1° alcohol formed is oxidised.

Observation for 2-bromo-2-methylpropane: Purple KMnO_4 remains as 3° alcohol formed cannot be oxidised.

[Test: 1 mark; observation: 1 mark]

[4]

- (c) An aromatic organic compound **A**, C_9H_{10} , decolourises bromine water and undergoes strong oxidation to give compound **B**, $\text{C}_8\text{H}_6\text{O}_4$. **B** forms intramolecular hydrogen bond.

A reacts with chlorine in the presence of sunlight to give compound **C**, $\text{C}_9\text{H}_9\text{Cl}$.

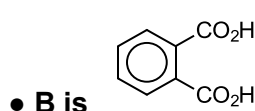
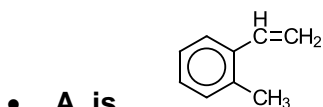
When **C** is heated under reflux with an ethanolic KCN followed by acid hydrolysis, compound **D** is formed. **D** liberates carbon dioxide with sodium carbonate.

Heating **D** under high pressure with a mixture of steam and phosphoric acid gives compound **E**. The resulting organic compound **E** gives a yellow solid with alkaline iodine solution.

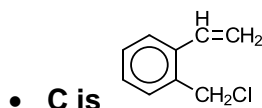
Heating **E** under reflux with concentrated sulfuric acid gives a sweet smelling compound **F**, $\text{C}_{10}\text{H}_{10}\text{O}_2$.

Use all the above information to identify the organic compound **A**, **B**, **C**, **D**, **E** and **F** and draw a structural formula for each of them. Clearly show all of the deductions that you make from the information that you have been given: full marks cannot be gained by only giving the structures required.

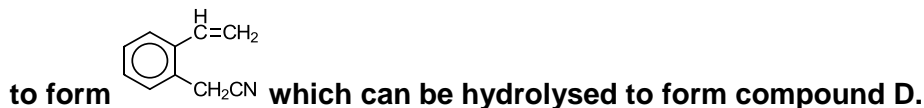
- **A decolourises bromine water** indicates **A** is an alkene, contains $>\text{C}=\text{C}<$ functional group.
- **A** undergoes oxidation to give compound **B**, $\text{C}_8\text{H}_6\text{O}_4$, which is a dicarboxylic acid & capable of forming intramolecular hydrogen bond. This indicates that 2 carboxylic group must be adjacent to each other. Hence, **A** also has 2 alkyl side chains which attach to benzene ring and they are adjacent to each other.



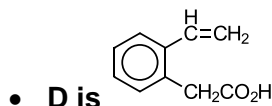
[1/2 Bonus] **A** undergoes free radical substitution reaction with chlorine in the presence of sunlight to give compound **C**, $\text{C}_9\text{H}_9\text{Cl}$. This indicates the presence of alkyl group, $-\text{CH}_3$, in **A**.



[1/2 Bonus] **C** undergoes nucleophilic substitution reaction with ethanolic KCN

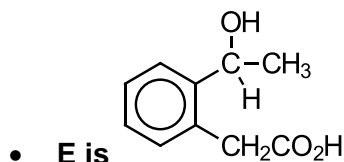


- **D is acidic** and has -CO₂H group, as it liberates CO₂ when reacts with sodium carbonate.

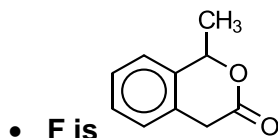


[1/2 Bonus] Heating D under high pressure with a mixture of steam and phosphoric acid, D undergoes electrophilic addition reaction, and compound E is obtained.

- E gives a yellow solid with alkaline iodine solution, E has group.



[1/2 Bonus] Heating E under reflux with concentrated sulfuric acid, E undergoes esterification to give a sweet smelling compound F, C₁₀H₁₀O₂ which is an ester.



[6 structures: 6 marks; explanation: 4 marks +2 bonus]

[10]
[Total: 20]