Section A

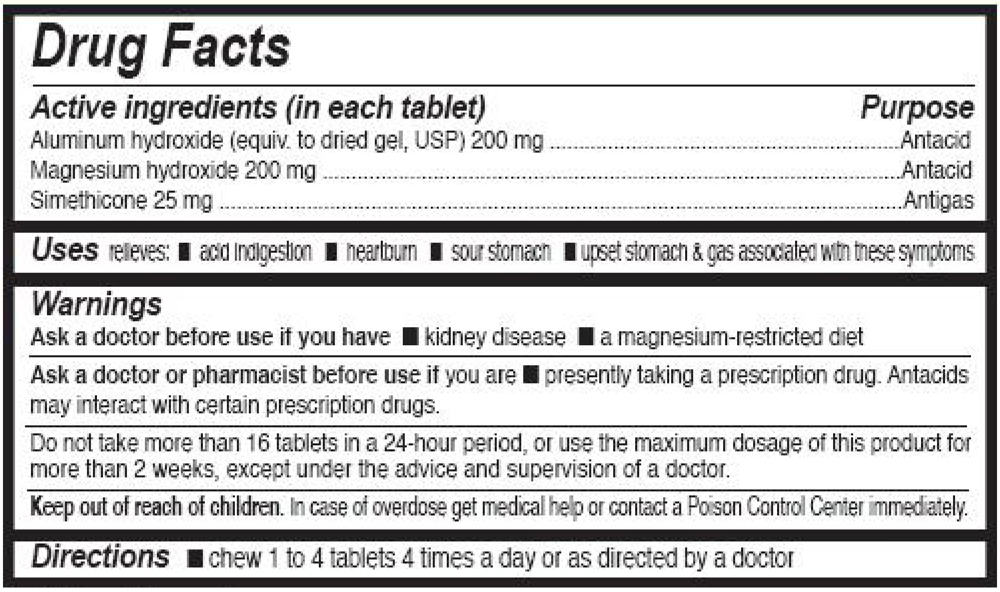
Answer **all** questions in this section in the spaces provided.

1 Aluminium is the most abundant Group 13 element and constitutes about 8% of the Earth's crust. The extraction of aluminium is done by processing aluminium ore, bauxite to produce aluminium oxide also known as alumina.

A variety of aluminium compounds, for example aluminium chloride and aluminium hydroxide, are used for different purposes such as food additives, colouring and pharmaceuticals.

Aluminium hydroxide and magnesium hydroxide are antacids. They are used to treat symptoms of increased stomach acid, such as heartburn, upset stomach, sour stomach, or acid indigestion. Once ingested, they react with the hydrochloric acid in the stomach.

One label of a commercial product, Mintox™ is shown below.



Drug Facts

Active ingredients (in each tablet)	*Purpose*
Aluminum hydroxide (equiv. to dried gel, USP) 200 mg	Antacid
Magnesium hydroxide 200 mg	Antacid
Simethicone 25 mg	Antigas

Uses relieves: ■ acid indigestion ■ heartburn ■ sour stomach ■ upset stomach & gas associated with these symptoms

Warnings

Ask a doctor before use if you have ■ kidney disease ■ a magnesium-restricted diet

Ask a doctor or pharmacist before use if you are ■ presently taking a prescription drug. Antacids may interact with certain prescription drugs.

Do not take more than 16 tablets in a 24-hour period, or use the maximum dosage of this product for more than 2 weeks, except under the advice and supervision of a doctor.

Keep out of reach of children. In case of overdose get medical help or contact a Poison Control Center immediately.

Directions ■ chew 1 to 4 tablets 4 times a day or as directed by a doctor

(a) **(i)** Write down the electronic configuration of A*l*. [1]

$1s^22s^22p^63s^23p^1$

(ii) Why is the ionic radius of aluminium far smaller than its atomic radius?

Al^{3+} ion has a higher proton to electron ratio, hence the remaining electrons experience stronger electrostatic forces of attraction to the nucleus.

In addition, Al^{3+} ion has one less principal quantum shell as compared to the neutral atom, hence the ionic radius is smaller than its atomic radius.

(iii) Explain why aluminium forms compounds with an oxidation state of +3 but not sodium. [1]

As compared to sodium, aluminium would require smaller amount of energy to remove the (2nd and 3rd) electrons which are from the outermost principle quantum shell.

(b) **(i)** Which antacid in the tablet is more effective in reacting with the hydrochloric acid in the stomach? Show relevant working to support your answer. [2]

Relevant working based on masses in the tablet

No of moles of $Mg(OH)_2$ = 200 x 10^{-3} / 58.3 = 3.43 x 10^{-3} mol
No of moles of $Al(OH)_3$ = 200 x 10^{-3} / 78 = 2.56 x 10^{-3} mol
$Al(OH)_3$ will produces more number of moles of hydroxide ions (7.68 x10^{-3}) than $Mg(OH)_2$(6.86 x10^{-3}) .

Thus aluminium hydroxide is more effective.

(ii) Calculate the maximum number of chewable tablets that a person can take in a week. [1]

4x 4 x 7 = 112

(iii) Assuming that a typical adult has a body mass of 70 kg, determine the maximum weekly intake of aluminium hydroxide in grams per kg of body mass. [2]

Maximum intake of aluminium hydroxide is 200 mg x 112

Maximum intake per body mass = 0.320 g per kg

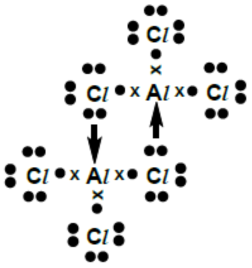
(c) **(i)** Aluminium chloride is an active ingredient used in skin medication to control excessive sweating.

Aluminium chloride is often describe as *electron deficient*. Explain what is meant by *electron deficient*. [1]

Electron deficient implies that the central atom, Al has empty orbital in $AlCl_3$

(ii) In the vapour phase, aluminium chloride forms a gaseous product with a molar mass of 267 g mol^{-1}. With an aid of a clearly labelled diagram, explain how this product is formed from aluminium chloride. [2]

Dative Bond



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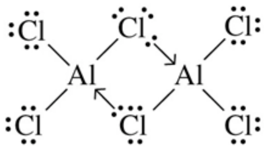


[Total: 11]

2 In a university laboratory, the percentage purity of a sample of complex iron salt, $K_3Fe(C_2O_4)_3.3H_2O$ can be determined by analyzing the $C_2O_4^{2-}$ content through titrating with acidified $KMnO_4$.

1.20 g of impure $K_3Fe(C_2O_4)_3.3H_2O$ sample was dissolved and made up to 100cm^3. 10.0 cm^3 of this solution was pipetted into a conical flask and 10.0cm^3 of 1 mol dm^{-3} sulfuric acid was added. The mixture was heated and titrated with 0.0200 mol dm^{-3} $KMnO_4$. CO_2 is produced during the reaction.

It was determined that 12.30 cm^3 of $KMnO_4$ was required to reach the end-point.

(a) **(i)** Suggest why hydrochloric acid is not used to acidify the mixture. [2]

Cl^- ions can possibly be oxidized to Cl_2 and hence will cause an increase in the titration readings.

(ii) In the acidic medium, $C_2O_4^{2-}$ ions exist as $H_2C_2O_4$.

Write a half equation to show the conversion of $H_2C_2O_4$ to CO_2. [1]

$H_2C_2O_4 \rightarrow CO_2 + 2H^+ + 2e$

(b) **(i)** Calculate the amount of $KMnO_4$ used to react with 10.0cm^3 of the iron complex salt solution. [1]

Amt of MnO_4^- = 12.3/1000 x 0.02 = 2.46 x 10^{-4} mol

(ii) Using the half-equation below and that in **(b)(ii)**, calculate the amount of $C_2O_4^{2-}$ present in 10.0 cm^3 of the iron complex salt solution.

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

[1]

Amount of e involved = 5 x 2.46 x 10^{-4}= 1.23 x 10^{-3}

Amount of $H_2C_2O_4$ = amount of $C_2O_4^{2-}$ = 5/2 x 2.46 x 10^{-4} = 6.15 x 10^{-4}

(iii) Hence, determine the mass of $K_3Fe(C_2O_4)_3.3H_2O$ in 100 cm^3 of iron complex salt solution.
(molar mass of $K_3Fe(C_2O_4)_3.3H_2O$ = 491.1 g mol^{-1}) [2]

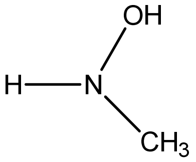
$K_3Fe(C_2O_4)_3.3H_2O \equiv 3C_2O_4^{2-}$
amount of $K_3Fe(C_2O_4)_3.3H_2O$ in 100cm^3 = 5/2/3 x 2.46 x 10^{-4} x 10
Mass of $K_3Fe(C_2O_4)_3.3H_2O$
= 5/2/3 x 2.46 x 10^{-4} x 10 x 491.1 = 1.01g

(iv) Calculate the percentage purity of the iron complex salt. [1]

1.01/1.20 x 100% = 84.2%

[Total: 8]

3 The emergence of multidrug-resistant bacteria has encouraged vigorous efforts to develop antibacterial agents. N-methylhydroxylamine has been found to show vast potential as an antibacterial agent.



N-methylhydroxylamine (pK_b = 8.04)

N-methylhydroxylamine has properties similar to ammonia and it dissolves in water as shown below:

$$CH_3NHOH(aq) + H_2O(l) \rightleftharpoons CH_3NH_2OH^+(aq) + OH^-(aq)$$

(a) Write the expression for the base dissociation constant of N-methylhydroxylamine in water. [1]

$$K_b = \frac{[CH_3NH_2OH^+][OH^-]}{[CH_3NHOH]}$$

(b) Calculate the base dissociation constant of the N-methylhydroxylamine solution. [1]

$K_b = 10^{-8.04} = 9.12 \times 10^{-9}$ mol dm^{-3}

An aqueous solution of 0.05 mol dm^{-3} hydrochloric acid was gradually added to 50.0 cm^3 of 0.02 mol dm^{-3} aqueous N-methylhydroxylamine.

(c) Determine the initial pH of N-methylhydroxylamine solution. [2]

$$CH_3NHOH(aq) + H_2O(l) \rightleftharpoons CH_3NH_2OH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[CH_3NH_2OH^+][OH^-]}{[CH_3NHOH]}$$

Since $[OH^-] = [CH_3NH_2OH^+]$,

$$K_b = \frac{[OH^-]^2}{[CH_3NHOH]}$$

$$9.12 \times 10^{-9} = \frac{[OH^-]^2}{0.02}$$

$[OH^-] = \underline{1.35 \times 10^{-5}}$ mol dm^{-3}

pH = 14 – [-log (1.48 × 10^{-5})]
= $\underline{9.13}$

(d) Calculate the volume of hydrochloric acid needed at the equivalence point. [1]

$CH_3NHOH + HCl \longrightarrow CH_3NH_2OH^+Cl^-$

Volume of HC*l* needed = (50.0 × 0.02) ÷ 0.05
= 20.0 cm^3

(e) State the volume of hydrochloric acid required to be added to another identical solution of N-methylhydroxylamine to obtain a solution which best resists pH change. [1]
10.0 cm^3

(f) Calculate the pH of that solution. [1]
$pOH = pK_b = 8.04$
$pH = 14-8.04 = 5.96$

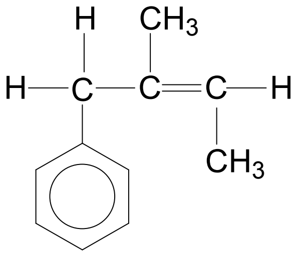
(g) Write **two** equations to show how the solution in **(e)** resists change in pH when small amounts of acid and alkali are added. [2]

$$CH_3NHOH + H^+ \longrightarrow CH_3NH_2OH^+$$

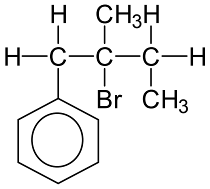
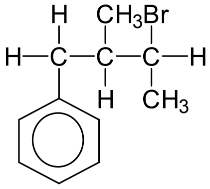
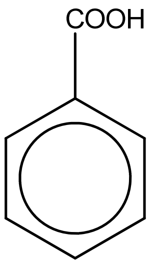
$$CH_3NH_2OH^+ + OH^- \longrightarrow CH_3NHOH + H_2O$$

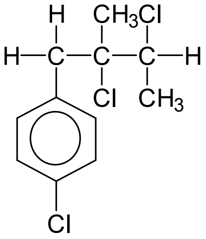
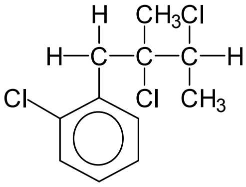
[Total: 9]

4 (a) Draw the structures of the organic product(s) formed when compound **A** below reacts with each of the following reagents.



compound **A**

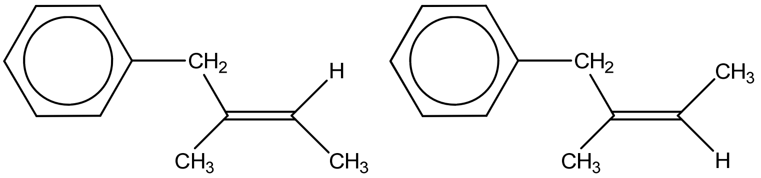
Reagents and Conditions	Organic Product(s) formed
(i) HBr(g)	Students to give either one of the correct structures  
(ii) $KMnO_4$; dilute H_2SO_4; heat under reflux	 + CH_3COOH

(iii) Cl_2(g); $AlCl_3$; dark	Students to give either one of the correct structures  

[5]

(b) State the type of isomerism exhibited by compound **A**, and hence draw the structures of the two isomers formed. **[2]**

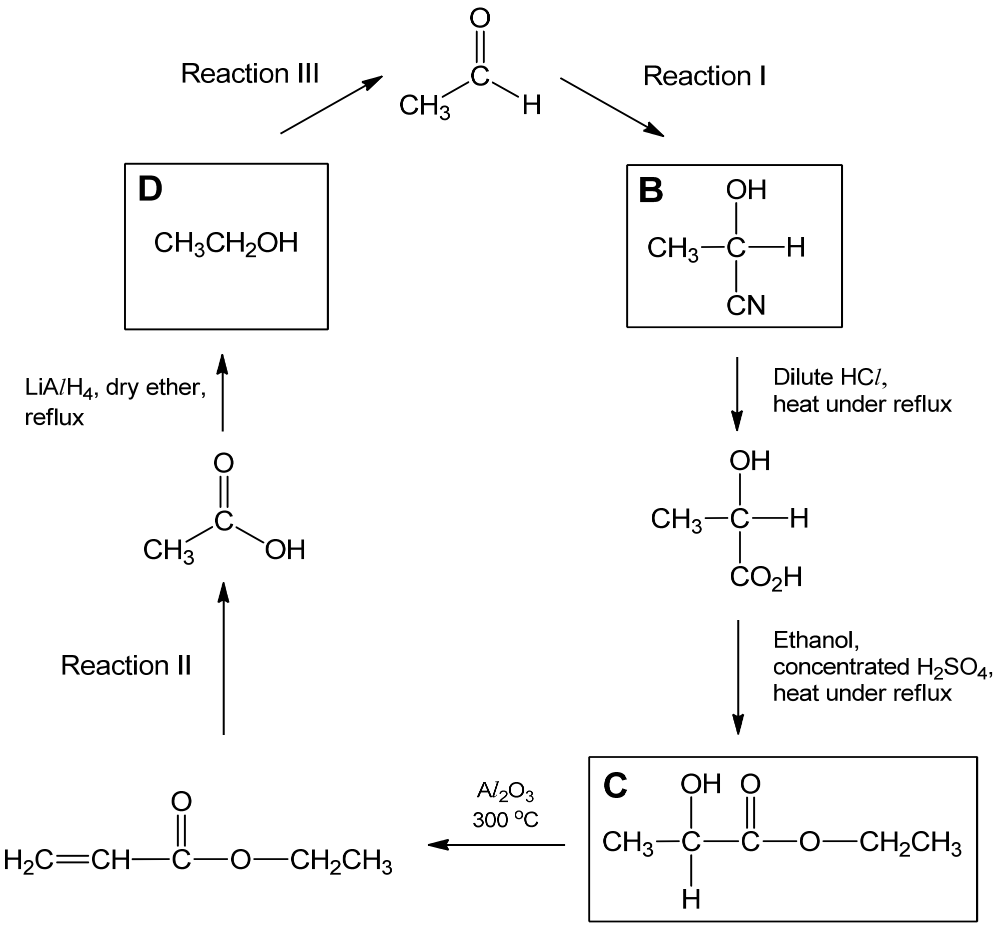
Cis-trans isomerism



cis trans

(c) Ethanal is a flammable liquid with a fruity smell. It occurs naturally in ripe fruit, coffee and fresh bread. A synthetic route involving ethanal is shown below.

(i) Draw the structural formulae of compounds **B**, **C** and **D** in the boxes below. **[3]**



(ii) Suggest reagents and conditions for

Reaction I, ...

Reaction II, ...

Reaction III, ...

[3]

[Total: 14]

- reaction I, HCN, trace amount of NaOH(aq), 10 to 20°C
  or HCN, trace amount of KCN, 10 to 20°C
- reaction II, $KMnO_4$, H_2SO_4(aq), heat under reflux
- reaction III, $K_2Cr_2O_7$, H_2SO_4(aq), heat and distill

Section B (40 marks)

Answer **two** questions from this section on the separate answer papers.

1 **(a)** In an experiment, the effect of reactant concentration on the rate of reaction between hydrogen peroxide and potassium iodide at 298K was investigated.

The rate of formation of iodine in the reaction:

$$H_2O_2(aq) + 2I^{-}(aq) + 2H^{+}(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

is given by:

$$\text{rate} = k[H_2O_2]^{a}[I^{-}]^{b}[H^{+}]^{c}$$

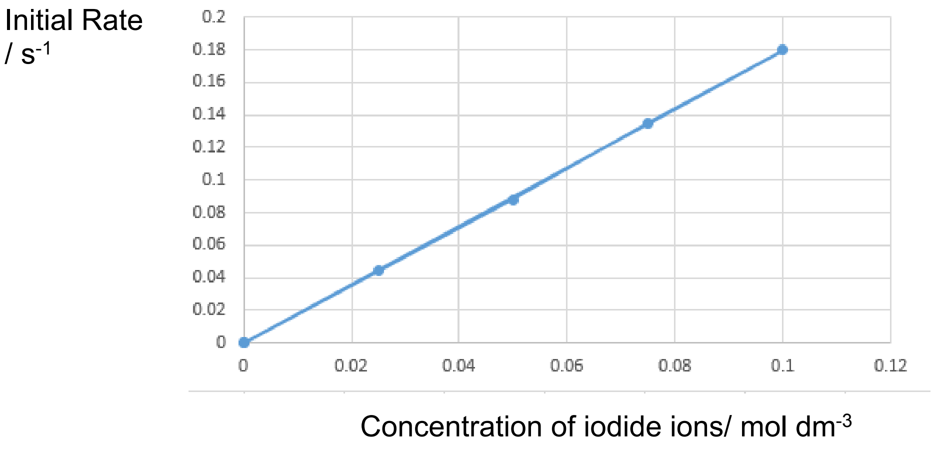
whereby a, b and c are the orders of reaction

The iodine liberated in the above reaction reacts with a fixed amount of sodium thiosulfate until no more sodium thiosulfate is left. The excess iodine causes the solution becomes coloured. By adding a few drops of starch, the iodine is shown up more clearly as it forms a blue-black complex.

The time taken for the formation of blue-black complex is measured. The reciprocal of this time ($\frac{1}{t}$) is used as a measure of the initial rate of reaction.

Concentration of KI/ mol dm^{-3}	Time/ s
0.10	5.5
0.075	7.4
0.050	11.3
0.025	22.7

(i) Plot a graph of initial rate against concentration of iodide ions. [3]



(ii) Hence use your graph to determine the order of reaction with respect to iodide ions. [1]

Clearly initial rate is directly proportional to the concentration. Thus it is first order.

(iii) In theory, the orders of reaction with respect to hydrogen peroxide and acid are one and zero respectively. [2]

Using your answer in **a(ii)** and given that $[H_2O_2] = 0.01$ mol dm^{-3}, $[I^-] = 0.02$ mol dm^{-3}, $[H^+] = 0.0005$ mol dm^{-3} and rate = 2.30×10^{-6} mol dm^{-3} s^{-1}, determine the rate constant for this reaction and state its units.

$$\text{rate} = k[H_2O_2][I^-]$$
$$2.30 \times 10^{-6} = k(0.01)(0.02)$$
$$k = 0.0115 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

(iv) Suggest what would happen to the initial rate of reaction if the temperature is changed to 308K. [1]

The rate would be doubled.

(b) **(i)** Describe the reactions, if any when separate samples of sodium and phosphorus are added to water containing universal indicator. [2]

Sodium dissolves in water to form an alkaline blue/violet solution and effervescence is seen.

Phosphorus does not react with water. Hence it forms a green solution in presence of universal indicator.

(ii) Explain the acid-base character of oxides of sodium and phosphorus in water. Suggest the pH of any aqueous solution formed. [2]

Sodium oxide is soluble in water to form an alkaline solution of aq NaOH.

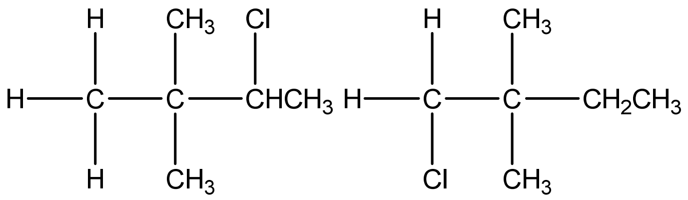
$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ pH =13

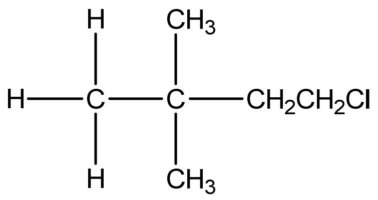
Phosphorus oxide is soluble in water to form an acidic solution of phosphoric acid.

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ pH =2

(c) When heated with chlorine under suitable conditions, hydrocarbon **X**, C_6H_{14} forms a total of only 3 mono-chlorinated products.

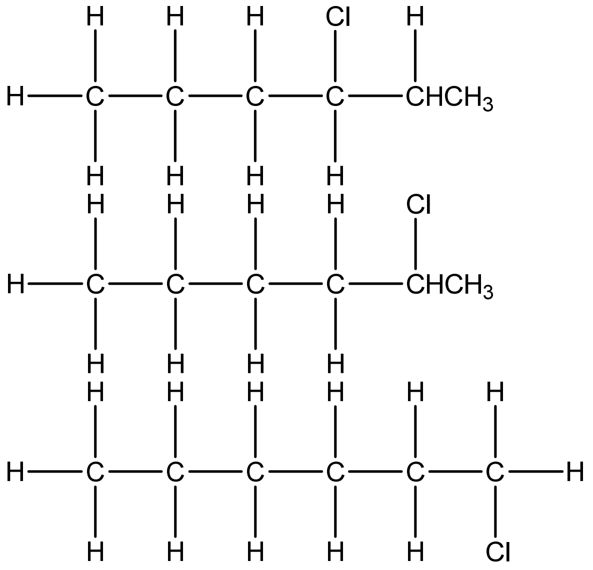
(i) Draw the three possible chlorinated products of **X**. [3]





$CH_3C(CH_3)_2CH_2CH_2Cl$

OR



$CH_3CH_2CH_2CHClCH_2CH_3$

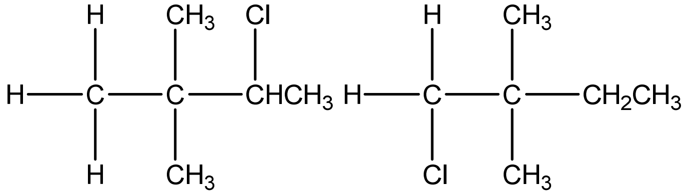
$CH_3CH_2CH_2CH_2CHClCH_3$

$CH_3CH_2CH_2CH_2CH_2CH_2Cl$

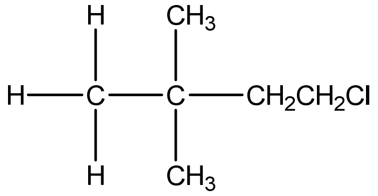
(ii) The following table provides the rate of abstraction of a hydrogen on a primary, secondary and tertiary carbon. [1]

Type of C	$-CH_3$	$-CH_2R$	$-CHR_2$
Relative rate	1	4	6

What is the expected ratio of the mono-chlorinated products of **X** formed?[2]



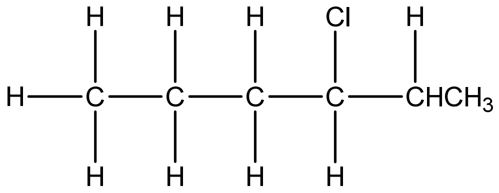
$CH_3C(CH_3)_2CHClCH_3$ $CH_2ClC(CH_3)_2CH_2CH_3$



$CH_3C(CH_3)_2CH_2CH_2Cl$

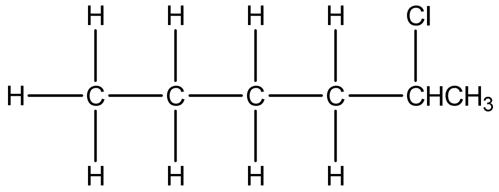
2X4 : 1x 9 : 3x1
8: 9: 3

OR



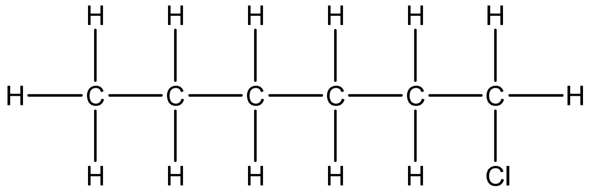
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-\overset{H}{C}HCH_3$$

4x 4 = 16



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{Cl}{C}HCH_3$$

4x 4=16



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H$$

6x 1=6
8: 8: 3

(iii) State one environmental effect of chlorinated products of **X**. [1]

Depletion of ozone layer

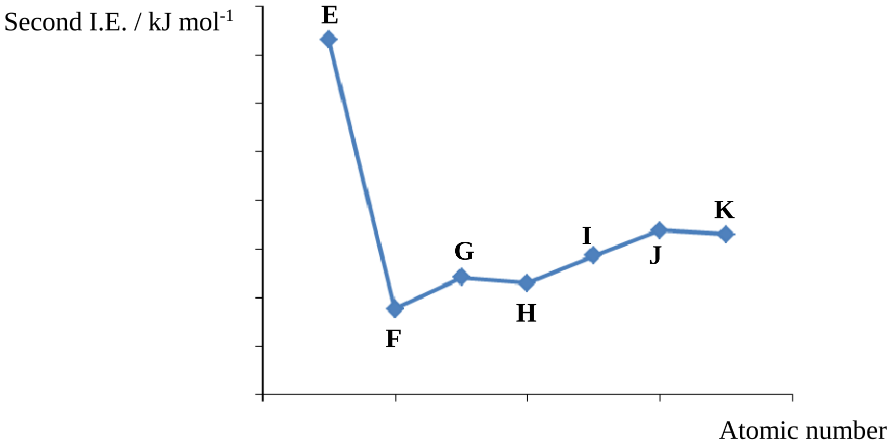
(iv) Describe a simple chemical test to distinguish the chlorinated products of **X** from hydrocarbon **X**. [3]

Aq NaOH, heat
Cool and add excess nitric acid
Lastly add silver nitrate solution

X: no white ppt
Chlorinated products: white ppt

[Total: 20 marks]

2 **(a)** Carbon forms the backbone of organic compounds and is in the Period 2 of the Periodic Table. The second ionisation energy of some consecutive elements in Period 2 are plotted.



(i) Write an equation to represent second ionisation energy of carbon. [1]

$C^+(g) \rightarrow C^{2+}(g) + e$

(ii) Considering electronic configurations, explain why the second ionisation energy of carbon is lower than that of boron. [2]

C^+ : $1s^2\,2s^2\,2p^1$

B^+ : $1s^2\,2s^2$

The second IE of carbon involves removing an electron from the 2p subshell, which is further away from the nucleus. Hence, less energy is required.

(iii) Which letter represents carbon in the plot? Explain your answer. [2]

H. There is a large difference between the second IE of E and F. This suggests that E is Li as the electron is removed from the inner principal quantum shell.

(b) Ethanoic acid and ethanol react together in the presence of concentrated sulfuric acid as the catalyst. The following equilibrium is established, in which the ester, ethyl ethanoate, is formed.

$$CH_3COOH\,(l) + CH_3CH_2OH\,(l) \rightleftharpoons CH_3COOCH_2CH_3\,(l) + H_2O\,(l)$$

(i) State Le Chatelier's Principle. [1]

Le Chatelier's Principle states that when a change is introduced into the system, the system will respond in such a way to counteract the change.

(ii) Use Le Chatelier's Principle to predict and explain how adding sodium hydroxide to the system will affect the position of equilibrium of this reaction. [2]

When sodium hydroxide is added, the concentration of ethanoic acid decreases. Hence, POE will shift to the left to counter this change.

(iii) Equimolar amounts of ethanoic acid and ethanol were mixed and at equilibrium, 1.00 mole of ethyl ethanoate is present. The total volume of the reaction mixture is 0.5 dm^3.

Given that the value of K_c for the reaction between ethanoic acid and ethanol is 4.0, determine the initial concentration of ethanoic acid. [3]

	CH_3COOH (l) +	CH_3CH_2OH (l) $\rightleftharpoons$	$CH_3COOCH_2CH_3$ (l) +	H_2O (l)
I / mol	x	x	0	0
C / mol	-1	-1	+1	+1
E / mol	x – 1	x-1	1	1

K_c = 1 / (x-1)(x-1) = 4

(x-1)(x-1) = ¼

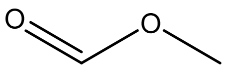
x -1 = ½

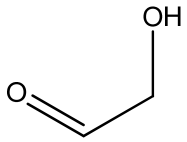
x = 1.5 mol

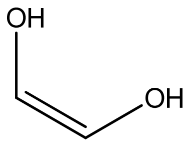
[ethanoic acid] = 1.5/0.5 = 3.00 mol dm^{-3}

(c) Other than ethanoic acid, there are other compounds that have the same molecular formula, $C_2H_4O_2$.

Give the skeletal formulae of **three** other possible isomers, with different functional groups from each other, which have this molecular formula. [3]







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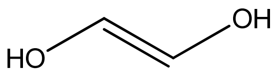

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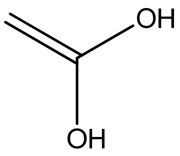


(d) In the laboratory, there are three bottles of chemicals which are unlabelled. The three bottles contain one of the following, but not in the order given.

Ethanoic acid

Propanone

Propanal

Suggest two simple chemical tests that will allow you to distinguish between the three unlabelled bottles. State clearly the observations and write equations for any reaction that occur. [6]

R & C: Na_2CO_3 (aq)

Observations: effervescence for ethanoic acid, no effervescence for propanone and propanal

Eqn: $2\ CH_3COOH + Na_2CO_3 \rightarrow 2\ CH_3COO^-Na^+ + CO_2 + H_2O$

R & C : $KMnO_4$ (aq), H_2SO_4 (aq), heat

Observations: purple $KMnO_4$ decolourised for propanal, purple $KMnO_4$ remains for propanone.

Eqn: $CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$

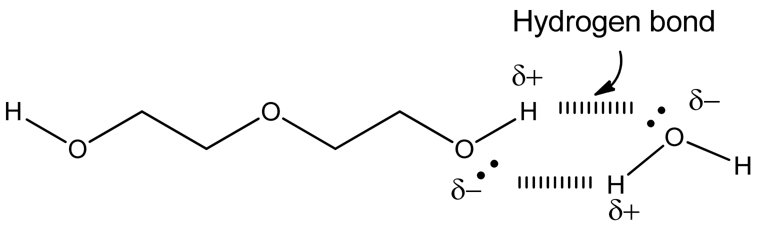
Accept any logical tests.

[Total:20]

3 Diethylene glycol (DEG), with the formula $(HOCH_2CH_2)_2O$, is used in a wide range of industrial products. It is poisonous and has been involved in a number of prominent mass poisonings spanning back to 1937.

(a) Following its ingestion, DEG is rapidly absorbed and distributed within the human body which is made up of up to 60% water.

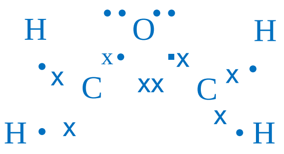
State and draw the type of bonding between DEG and water. [3]



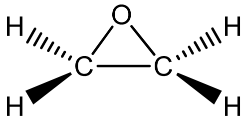
(b) DEG is produced by the hydrolysis of the cyclic ethylene oxide, $(CH_2)_2O$.

$2\ (CH_2)_2O + H_2O \rightarrow HO–CH_2CH_2–O–CH_2CH_2–OH$

(i) The oxygen atom is bridging the two carbon atoms in the cyclic ethylene oxide. Draw the 'dot-and-cross' diagram of ethylene oxide showing all bonding electrons and non-bonding electrons clearly. [1]



(ii) Give a value for the bond angle around the oxygen atom in ethylene oxide molecule. [1]



60 °

(iii) Predict and explain whether ethylene oxide would be more soluble in propanone or hexane. [2]

Propanone

Ethylene oxide is polar and dissolves well in polar solvent such as propanone through permanent dipole-permanent dipole interaction

(iv) Use the *Data Booklet* to calculate the enthalpy change when ethylene oxide is hydrolysed showing clearly which bonds are broken and formed in the above equation. [3]

Bonds broken = 2 (O-H) +2(C-O)
Bonds formed = 2 (O-H) +2(C-O)

$\Delta H = 0 \text{ kJ mol}^{-1}$

(c) An organic compound **P**, $C_{10}H_{11}O_2Br$, does not react with aqueous sodium carbonate. However, it reacts slowly on heating in aqueous sodium hydroxide to form a water-soluble compound **Q**, $C_3H_5O_3Na$ and an insoluble oil **R**, C_7H_8O.

The acidification of compound **Q** gives compound **S** which reacts with 2 moles of phosphorous pentachloride to give copious fumes. **R** gives benzoic acid on oxidation.

Deduce the structures of compounds **P**, **Q**, **R** and **S**. Explain the chemistry of the reactions described, writing equations where appropriate. [10]

Compound **P** does not react with Na_2CO_3(aq). Hence, compound **P** is not a carboxylic acid.

Compound **P** undergoes alkaline hydrolysis when heated with NaOH(aq). **P** has alkyl halide functional group. The Br atom in compound **P** is substituted by –OH.

Compound **Q**, $C_3H_5O_3Na$, and compound **R**, C_7H_8O, were produced upon alkaline hydrolysis. Ester linkage present in compound **P**.

Q has an alcohol functional group. The acidification of compound **Q** gives compound **S** which reacts with 2 moles of phosphorous pentachloride to give copious fumes. Compound **S** is an alcohol and carboxylic acid.

Compound **R** gives benzoic acid on oxidation. Compound **R** contains a benzene ring with a side chain, (oxidation of side-chain) **R** has an alcohol group.

$C_6H_5CH_2OCOCH(Br)CH_3 + 2NaOH \longrightarrow CH_3CH(OH)COONa + C_6H_5CH_2OH + NaBr$

$C_6H_5CH_2OH + 2[O] \longrightarrow C_6H_5COOH + H_2O$

$CH_3CH(OH)COONa + H^+ \longrightarrow CH_3CH(OH)COOH + Na^+$

$CH_3CH(OH)COOH + 2PCl_5 \longrightarrow CH_3CH(Cl)COCl + 2HCl + 2POCl_3$

P is $C_6H_5CH_2OCOCH(Br)CH_3$ or $C_6H_5CH_2OCOCH_2CH_2Br$
Q is $CH_3CH(OH)COONa$ or $CH_2(OH)CH_2COONa$
R is $C_6H_5CH_2OH$
S is $CH_3CH(OH)COOH$ or $CH_2(OH)CH_2COOH$

[Total: 20]

End of Paper