Section A

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

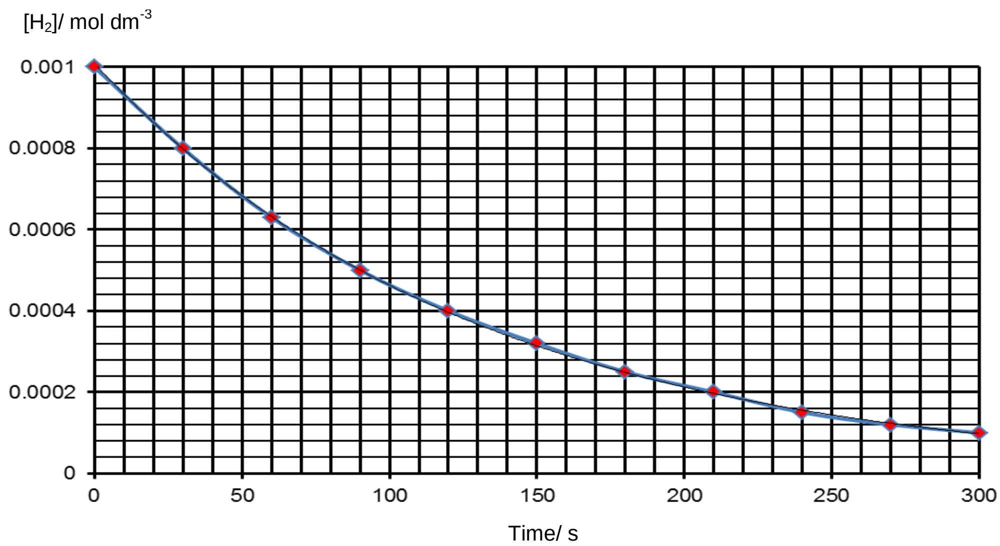
For Examiner's use

1 Oxides of nitrogen are by-products of combustion of hydrocarbon fuels in internal combustion engines. One of them is nitrogen monoxide.

At 700 °C, nitrogen monoxide and hydrogen react as follows:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O\,(g)$$

Keeping the concentration of nitrogen monoxide to be constant at 0.012 mol dm^{-3}, the following graph was obtained.



(a) **(i)** Calculate its initial rate of this reaction. **[1]**

Initial rate = 6.67 x 10^{-6} mol dm^{-3} s^{-1}

(ii) The results of some investigation of the rate of reaction are shown below. **[1]**

Experiment Number	Initial [NO]/ mol dm^{-3}	Initial $[H_2]$/ mol dm^{-3}	Initial Rate/ x 10^{-6} mol dm^{-3} s^{-1}
1	0.0120	0.002	13.0

Using the given information and your answer in **(i)**, determine the order of reaction with respect to hydrogen.

Comparing experiment 1 and keeping initial [NO] constant, the initial rate doubles when the initial $[H_2]$ doubles, hence order of reaction wrt H_2 is 1.

(iii) Using the information below, deduce the order of reaction with respect to NO. Show your working clearly. **[2]**

Experiment Number	Initial [NO]/ mol dm^{-3}	Initial $[H_2]$/ mol dm^{-3}	Initial Rate/ x 10^{-6} mol dm^{-3} s^{-1}
2	0.0020	0.012	2.2
3	0.0040	0.012	8.7

$$\frac{\text{Rate 2}}{\text{Rate 3}} = \frac{k(0.012)(0.0020)^x}{k(0.012)(0.0040)^x}$$

$$\frac{2.2\text{x}10^{-6}}{8.7\text{x}10^{-6}} = \left(\frac{1}{2}\right)^x$$

x = 2

(iv) Determine a value of *k*, stating the units. **[2]**

Using experiment 1,
$13 \times 10^{-6} = k(0.012)^2(0.0020)$
$k = 45.1\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$

(b) Write equations including state symbols for the reaction of the following oxides with water. In each case, state the pH of the resulting solution.

(i) Na_2O **[1]**

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

(ii) P_4O_6 **[1]**

$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$ pH 2 or 3

[Total: 8 marks]

2 During the OPEC 1973 oil crisis, methanol from coal is proposed as a proven liquid fuel with well-established manufacturing technology and sufficient resources to replace gasoline. The enthalpy of combustion of methanol in a typical car engine is -715 kJ mol^{-1}.

For Examiner's use

In a methanol plant, its production is carried in 2 steps. The first step is to convert the feedstock natural gas into a synthesis gas stream consisting of carbon monoxide, carbon dioxide, steam and hydrogen.

Methanol can then be produced by using the following reversible reaction between carbon monoxide and hydrogen.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

(a) **(i)** It is recommended that the temperature of a stationery or slow moving car should reach the optimum temperature of 34.0 °C before acceleration to 80 km per hour should take place to achieve optimum fuel efficiency. **[3]**

The efficiency of energy transfer in the engine from the combustion of fuel is 95% and the mass of engine oil found in the engine is 2.5 kg.

Calculate the mass of methanol that should be burnt in order to for the car to reach its optimum temperature from an initial temperature of 20.0 °C.

Given that the specific heat capacity of engine oil is 1.8 kJ K^{-1} kg^{-1}.

Heat required to raise to optimum temperature

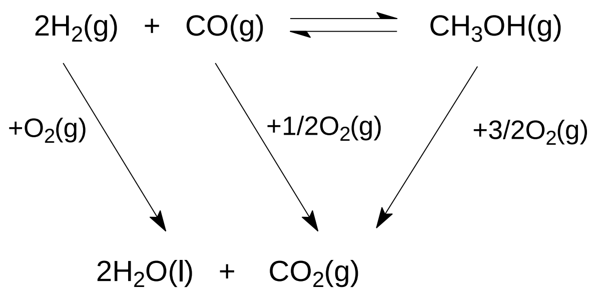
= 2.5 x 1.8 x (34.0 – 20.0)= 63 kJ

No. of moles of methanol = 63 / 715 (0.95) = 0.09275 mol

Mass of methanol = 0.09275 x 32.0 = 2.97 g

(ii) Given the following standard enthalpy change of combustion data and energy cycle, apply Hess's Law and calculate the enthalpy change for the production of methanol using carbon monoxide and hydrogen. **[2]**

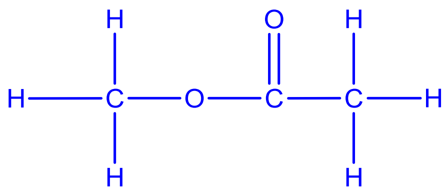
$\Delta H_c^{\theta}(H_2)$ = – 286 kJ mol^{-1}
$\Delta H_c^{\theta}(CO)$ = – 283 kJ mol^{-1}



$\Delta H_{reaction} = 2\Delta H_1 + \Delta H_2 - \Delta H_3$
$= 2(-286) - 283 - (-715)$
$= -140$ kJ mol^{-1}

(iii) Compound **A** can be used as low toxicity solvent in paints, glues and nail polish remover. It can be synthesized using methanol and ethanoic acid in the presence of concentrated sulfuric acid. **[2]**

Draw the displayed formula of compound **A** and state the type of reaction.



Condensation/esterification

(b) Methanol can be used to determine the concentration of iron in an impure solid.

7.00 g of the impure solid was first dissolved in an excess of sulfuric acid and completely oxidised to form Fe^{3+} (aq) solution. The resulting solution containing Fe^{3+} was made up to 250 cm^3.

10.0 cm^3 of this solution was titrated against a solution of methanol of concentration 0.01 mol dm^{-3}. During the titration, effervescence was observed. The gas evolved formed white precipitate in $Ca(OH)_2$ (aq).

It was found that 24.00 cm^3 methanol was required and Fe^{3+} is reduced to Fe^{2+} upon complete reaction. The half equation of the reduction of Fe^{3+} is:

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

(i) Write a balanced oxidation half equation of methanol. **[1]**

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e$

(ii) Write a balanced redox equation with state symbol for the reaction between Fe^{3+} and CH_3OH. **[1]**

$6\ Fe^{3+}(aq) + CH_3OH\ (aq) + H_2O(l) \rightarrow 6Fe^{2+}(aq) + CO_2\ (g) + 6H^+(aq)$

(iii) Calculate the percentage purity of iron in the impure solid. **[3]**

No. of moles of CH_3OH used = $24.00 \times 10^{-3} \times 0.01 = 2.4 \times 10^{-4}$ mol

No. of moles of Fe^{3+} in 10.0 cm^3 = $6 \times 2.4 \times 10^{-4} = 1.44 \times 10^{-3}$ mol

No. of moles of Fe^{3+} in 250 cm^3 = $1.44 \times 10^{-3} \times 250/10 = 0.0360$ mol

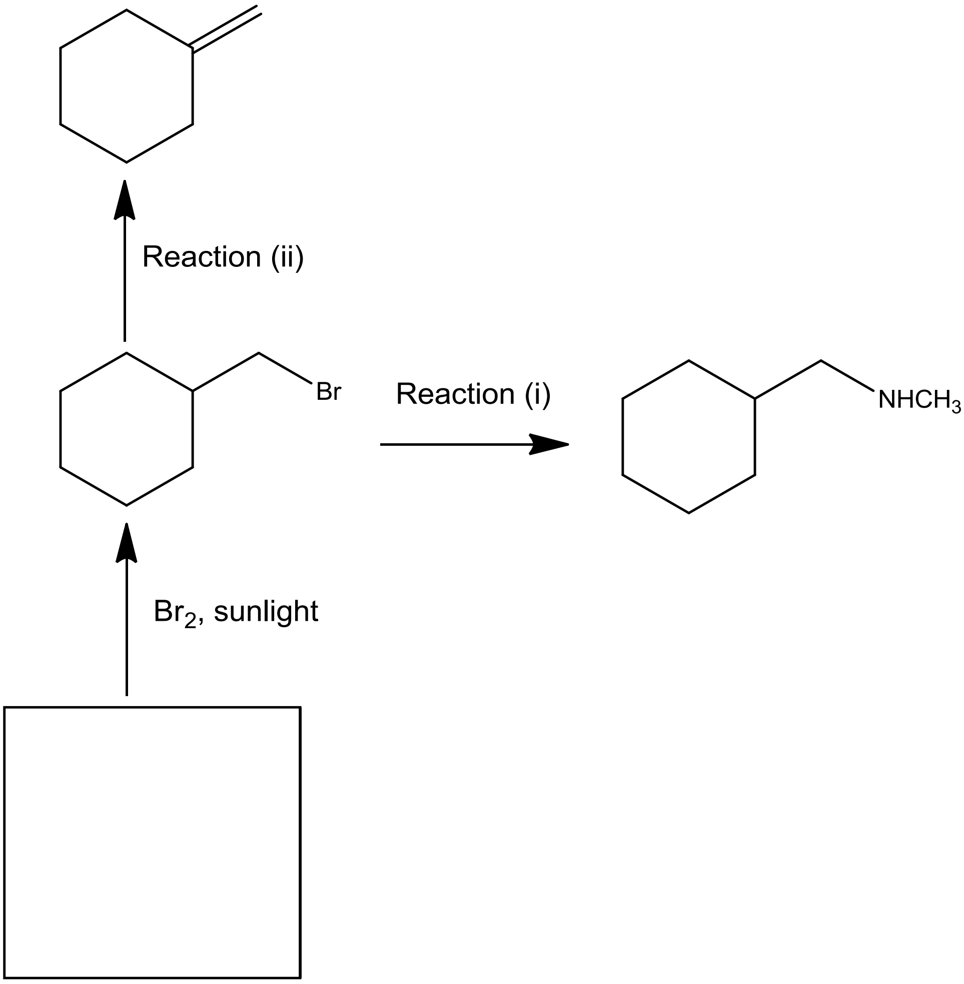
Mass of Fe in sample = $0.0360 \times 55.8 = 2.009$ g

% of Fe in sample = $2.009/7.00 \times 100 = 28.7\%$

[Total: 12 marks]

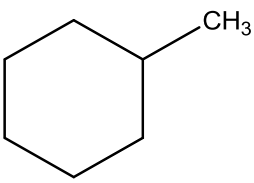
For Examiner's use

3 (a) Compound **Z** is a component found in aviation fuel. Some chemical transformations of Compound **Z** are given below.



Compound **Z**

(i) Draw the structural formula of Compound **Z**. **[1]**



(ii) State the reagents and conditions used in reaction (ii). **[1]**

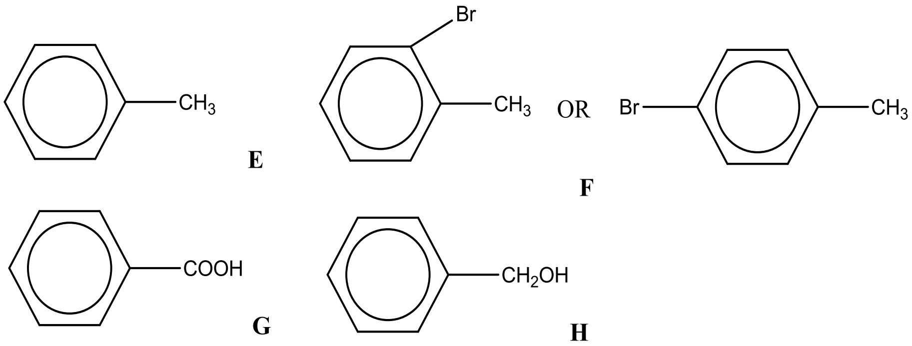
Ethanolic NaOH, heat with reflux

(iii) State the type of reaction for reaction (i) and (ii). **[2]**

Reaction (i) : Substitution
Reaction (ii) : Elimination

(b) Compound **E**(C_7H_8) is an essential starting material for organic chemistry synthesis. When **E** reacts with bromine in presence of iron, it forms compound **F**. Compound **G** can be obtained from **E** under suitable condition with manganate(VII) solution.

Compound **G** and **H** produce effervescence when reacted with sodium. **G** dissolves in aqueous sodium hydroxide but **H** cannot. **G** can be obtained from **H** from treatment with hot acidified potassium dichromate. Suggest the structures for **E**, **F**, **G** and **H**. **[4]**



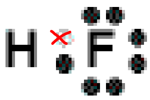
[Total: 8 marks]

4 Data about HF, HC*l*, HBr and HI are given below.

For Examiner's use

	HF	HC*l*	HBr	HI
Boiling Point / ^{o}C	20	-85	-67	-35
Bond Energy / kJ mol^{-1}	562	431	366	299

(a) **(i)** Draw the dot-and-cross diagram to illustrate the bonding in HF. **[1]**



(ii) Hence, explain why the bond energy of the hydrogen halides decreases down the group. **[1]**

- As the size of the halogen atom increases, effectiveness of the overlap of the bonding orbitals decrease

(iii) Whilst the bond energy of the hydrogen halides shows a neat trend, the bond energy of the halogens do not. Based on the data available from your data booklet, identify the halogen that does not fit in with the trend and suggest an explanation for the irregularity. **[2]**

- Fluorine
- Non bonding pairs of electrons on the fluorine atoms are too close resulting in repulsion and thus weakening the bond.

(b) **(i)** Explain why the boiling points of HC*l*, HBr and HI increase down the group. **[1]**

- As molecular size increases, the VDW strength increases

(ii) Suggest why the boiling point of HF is much higher than those of the others. **[1]**

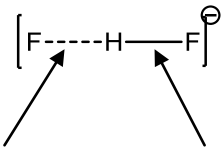
- Unlike the other hydrogen halides, hydrogen bonding between HF molecules is very strong

(c) HF reacts with potassium hydroxide to form an ionic compound, KHF_2, containing one cation and one anion.

(i) Write the formulae of the ions present in KHF_2 **[2]**

- K^+
- HF_2^-

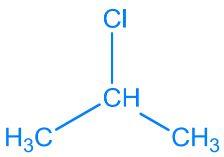
(ii) Suggest a structure for the anion and state what type(s) of bonding occur within it. **[2]**

- 

Hydrogen bonding   Covalent bonding

(d) HC*l*(g) is produced by adding concentrated sulfuric acid to solid sodium chloride, which can then be used to produce organic halogen compounds. State the type of reaction and draw the structural formula of the product formed when HC*l*(g) is reacted with the following.

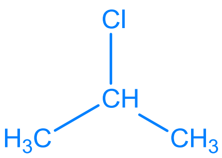
(i) Propene **[1]**



Addition

(ii) Propan-2-ol **[1]**

Substitution



[Total: 12 marks]

Section B

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

5 **(a)** NO_2 can be obtained by the reversible reaction between NO and O_2. The equation for the reaction is

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

In a particular reaction, there are 0.480 moles of oxygen and 0.760 moles of nitrogen monoxide was sealed together in a container of volume 1.50 dm^3. When the equilibria mixture was achieved at 400 °C and 100 atm, it was found that 0.140 moles of oxygen was consumed.

(i) Use the information above to calculate the value of K_c. State its units. **[2]**

	O_2(g)	+ 2NO(g)	$\rightleftharpoons$	$2NO_2$ (g)
Initial moles/mol	0.480	0.760		0
Change/mol	-0.140	-0.280		+0.280
Equilibrium moles/mol	0.340	0.480		0.280

$$Kc = \frac{\left(\frac{0.280}{1.50}\right)^2}{\left(\frac{0.480}{1.50}\right)^2\left(\frac{0.340}{1.50}\right)} = 1.50\ mol^{-1}\ dm^3$$

(ii) When the temperature was decreased to 200 °C, it was found that 0.200 moles of oxygen was consumed. Deduce whether the reaction is endothermic or exothermic. **[1]**

When temperature decreases, the larger amount of oxygen used implies that the position lies to the right. Low temperature favours exothermic reaction which is the forward reaction.

(iii) Explain whether the equilibrium constant, K_c will be affected when the original amount of reactants is halved. **[1]**

Kc is not affected as Kc is temperature dependent.

(b) Hydrazine is commonly used as rocket fuel as it does not produce carbon dioxide. In the combustion chamber of the rocket, hydrazine is passed over a suitable catalyst and decomposes to its constituent elements. The rapid production of the hot gaseous elements provides the thrust. Ammonia is usually an intermediate in the decomposition.

(i) Hydrazine is produced between the reaction of ammonia and hydrogen peroxide. **[2]**

$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H = -241.0\ kJ\ mol^{-1}$

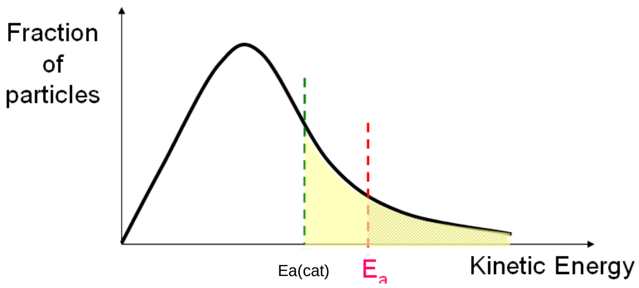
The standard enthalpy changes of formation are
NH_3: $-46.1\ kJ\ mol^{-1}$, H_2O_2: $-187.8\ kJ\ mol^{-1}$, H_2O: $-285.8\ kJ\ mol^{-1}$

Hence calculate the standard enthalpy change of decomposition of hydrazine.

$(2x\text{-}285.8) + \Delta H - (2x\text{-}46.1) - (1x\text{-}187.8) = -241.0$
$\Delta H = +50.6 \text{ kJ mol}^{-1}$

Enthalpy change of decomposition = - 50.6 kJ mol^{-1}

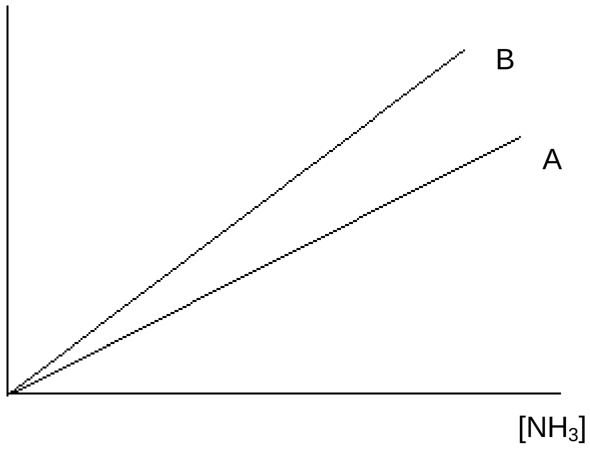
(ii) In a study, the kinetics of reaction between ammonia and hydrogen peroxide have been investigated. It is found that the activation energy deceases in presence of iron(II) ions. With the aid of a Boltzmann distribution curve, explain the effect of iron(II) ions on the rate of reaction. **[3]**



Iron(II) ions provides an alternative reaction pathway which lowers the activation energy of the reaction. Thus fraction of particles with energy ≥ Ea increases. Frequency of effective collisions increases and hence reaction rate increases.

(iii) It has been found that the order of reaction with respect to ammonia is first order. Assuming that hydrogen peroxide is in large excess, sketch the graph of rate against [NH_3] without adding iron(II) ions. Label this as graph A. On the same axes, sketch the graph that represents the reaction with addition of iron(II) ions. Label this as graph B. **[2]**

Rate



(c) The following table compares the pK_a values of various organic compounds.

	pK_{a1}	pK_{a2}
Malonic acid, $CH_2(COOH)_2$	2.85	5.70
Methanoic acid, HCOOH	3.77	-
Methanol, CH_3OH	15.5	-

(i) Explain why methanoic acid has a lower pK_a value than methanol. **[1]**

Methanoic acid contains a carboxylic acid. Carboxylate anion stabilized by delocalization of the electrons over the carbon atom and both oxygen atoms.

(ii) Suggest a reason why the pKa_2 value of malonic acid is greater than its pK_{a1} value. **[1]**

It is difficult to remove the H^+ ion from a negatively charged ion. Hence less acidic.

(d) **(i)** Sodium hydrogen carbonate is often used to neutralise methanoic acid present in ant sting. In a typical ant sting, the ant injects 6.0×10^{-3} cm^3 of solution containing 40% methanoic acid by volume under the skin. Determine the mass of sodium hydrogen carbonate needed for this treatment given the density of methanoic acid to be 1.2 g cm^{-3}. **[2]**

Volume of methanoic acid = $0.40 \times 6 \times 10^{-3} = 2.4 \times 10^{-3}$ cm^3

Mass of methanoic acid = $1.2 \times 2.4 \times 10^{-3} = 2.88 \times 10^{-3}$ g

Number of moles of methanoic acid = Number of moles of sodium hydrogen carbonate = $2.88 \times 10^{-3}/46 = 6.26 \times 10^{-5}$ mol

Mass of sodium hydrogen carbonate = $6.26 \times 10^{-5} \times (84) = 5.26 \times 10^{-3}$ g

(ii) Suggest a 3-step synthesis route to make methanoic acid, HCOOH from ethanol. Write down all reagents and conditions and draw any intermediates. **[5]**

$$CH_3CH_2OH \longrightarrow CH_3CHO \longrightarrow HCOO^-Na^+$$

$$\downarrow$$

$$HCOOH$$

1. K_2CrO_7, dilute sulfuric acid, heat with distillation
2. Aq I_2, aq NaOH, warm
3. Dilute HCl or Dilute H_2SO_4

[Total: 20 marks]

6 (a) Carbolic acid is a versatile precursor to a large collection of pharmaceutical drugs such as aspirin. It behaves as a monoprotic acid and does not have carboxylic acid functional group. A solution of carbolic acid in water has a concentration of 2.50 mol dm^{-3} and a pH of 5.4.

(i) Explain, with the aid of appropriate calculations, whether carbolic acid is a strong or weak acid. **[2]**

$[H^+] = 10^{-5.4} = 3.98 \times 10^{-6}$ mol dm^{-3}

Carbolic acid is a weak acid as $[H^+]$ is much lower than the concentration of the carbolic acid solution.

(ii) Use the data given to calculate the value of K_a of carbolic acid. **[1]**

$K_a = [H^+]^2 / [HA] = (3.98 \times 10^{-6})^2 / (2.50 - 3.98 \times 10^{-6}) = 6.34 \times 10^{-12}$ mol dm^{-3}

(iii) Suggest a suitable indicator for the titration of carbolic acid with aqueous sodium hydroxide. **[1]**

Phenolphthalein

(iv) A sample of carbolic acid of mass 1.34 g was dissolved in water and titrated with 0.500 mol dm^{-3} sodium hydroxide solution. It was found that 28.5 cm^3 of sodium hydroxide was required for neutralisation. Calculate the M_r of carbolic acid. **[2]**

Amt of sodium hydroxide used = (28.5 / 1000) x 0.500 = 0.01425 mol.

carbolic acid: NaOH = 1:1

Amt. of carbolic acid = 0.01425 mol

M_r of carbolic acid = 1.34/0.01425 = 94.0

(v) The percentage by mass of C, H and O in carbolic acid is 76.6%, 6.4% and 17.0% respectively. **[3]**

Determine the empirical formula and molecular formula of carbolic acid. Deduce the structural formula of carbolic acid.

Element:	C	H	O
% by mass:	76.6	6.4	17.0

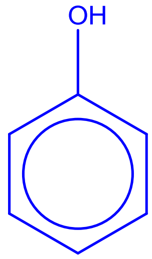
% by mass/Ar:	76.6/12.0	6.4/1.0	17.0/16.0
	= 6.383	= 6.400	= 1.0625
Simplest ratio:	6	6	1

Empirical formula: C_6H_6O

M_r of $(C_6H_6O)_n = 94.0$

$n(72.0 + 6.0 + 16.0) = 94.0 \therefore n = 1$

Molecular formula = C_6H_6O



(b) A buffer solution is prepared using 80 cm^3 of 0.10 mol dm^{-3} acetic acid, CH_3COOH and 40 cm^3 of 0.10 mol dm^{-3} sodium hydroxide, NaOH.

(i) What do you understand by the term *buffer solution*? **[1]**

A buffer is a solution that maintains a fairly constant pH upon adding of a small amount of acids or alkalis.

(ii) Write equations to show how this buffer solution reacts with **[2]**

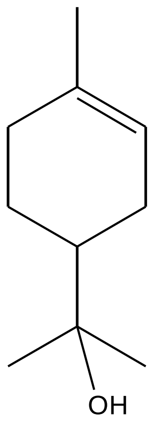
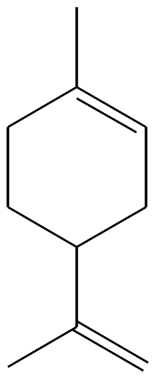
1. H^+ (aq) added

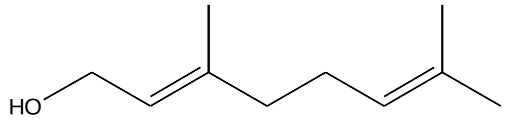
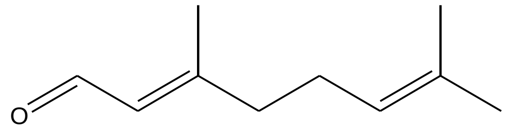
2. OH^- (aq) added

$H^+ + CH_3COO^- \rightarrow CH_3COOH$

$OH^- + CH_3COOH \rightarrow CH_3COO^- + H_2O$

(c) Terpineol and limonene are members of a class of compounds called terpenes and geraniol and citral belong to a class of compounds called terpenoids. They are widely found in nature.

	
Terpineol	**Limonene**

	
Geraniol	**Citral**

(i) Identify the functional groups present in geraniol and citral. **[2]**

Geraniol: alkene and primary alcohol

Citral: alkene and aldehyde

(ii) State the reagents and conditions to synthesize citral from geraniol. **[1]**

Acidified potassium dichromate, heat with distillation.

(iii) State the reagents and conditions to synthesize limonene from terpineol. **[1]**

Concentrated sulfuric acid, 170 ^{0}C or Al_2O_3, heat

(iv) Describe, by means of simple chemical tests, how you would distinguish between the following pairs of compounds. **[4]**

(I) Terpineol and Limonene

(II) Geraniol and Citral

Terpineol and limonene

Add PCl_5.

White fumes of HCl observed for terpineol but not for limonene.

OR

Add hot acidified potassium manganate(VII).

Purple potassium manganate (VII) decolourised for both compounds. Colourless odourless gas that gives a white precipitate with limewater produced for limonene but not for terpineol.

Geraniol and citral

Add 2,4-DNPH with warming. Orange ppt formed for citral but not geraniol.

OR

Add PCl_5.

White fumes of HCl formed for geraniol but not for citral.

OR

Add Tollen's reagent with warming. Silver mirror formed for citral but not geraniol.

[Total: 20 marks]

7 **(a)** The chlorides of the elements sodium to phosphorus all dissolve in or react with water.

(i) State the formula of a chloride of each of these five elements. **[2]**

- $NaCl$, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_3 or PCl_5

(ii) Describe the reaction, if any, of the chlorides of sodium and silicon with water. Give equation for any reactions and suggest the pH values of the resulting solutions. **[3]**

NaCl dissolves to form a colourless solution, pH = 7

$NaCl + aq \rightarrow Na^+ + Cl^-$

$SiCl_4$ hydrolyses completely to form a white solid and a strongly acidic solution, pH = 2

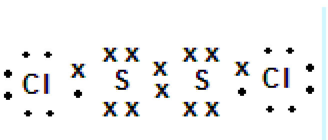
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

(b) A chloride of a group V element has the formula MCl_3. When 0.10g of MCl_3 was added to water and the resulting solution titrated with 0.050 mol dm^{-3} silver nitrate, it was found that 33.0 cm^3 of aqueous silver nitrate were needed to precipitate all the chloride ions. Based on these data, calculate the Ar of M and hence identify M. **[3]**

$nCl^- = 33 \times 10^{-3} \times 0.05 = 0.00165$
$nMCl_3 = 0.00165/3 = 0.00055$
$Mr = 0.1/0.00055 = 181.8$
$Ar = 181.8 - 3(35.5) = 75.3$
M is As

(c) Sulfur and chlorine can react together to form S_2Cl_2. When 1.00g of this sulfur chloride reacted with water, 0.36g of a yellow precipitate was formed, together with a solution containing a mixture of sulfurous acid, H_2SO_3, and hydrochloric acid.

(i) Draw the dot-and-cross diagram to show the bonding in S_2Cl_2. Suggest the approximate bond angles about the sulfur atoms in both S_2Cl_2 and H_2SO_3 accounting for any differences in the bond angles. **[3]**



104.5^o for S_2Cl_2 having 2 BP & 2LP
107^o for H_2SO_3 having 3BP & 1LP

(ii) Use the above data to deduce the equation for the reaction between S_2Cl_2 and water. **[2]**

$2S_2Cl_2 + 3H_2O \rightarrow 3S + H_2SO_3 + 4HCl$

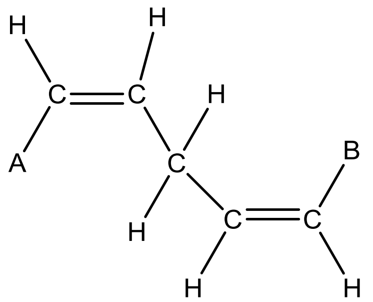
What volume of 1.00 mol dm^{-3} sodium hydroxide would be required to neutralise the final solution completely? **[2]**

$nS_2Cl_2 = 0.00740$
$nH^+ = 0.00740 \times 6 = 0.0444$
Vol of NaOH = 0.0444 dm^3 = 44.4 cm^3

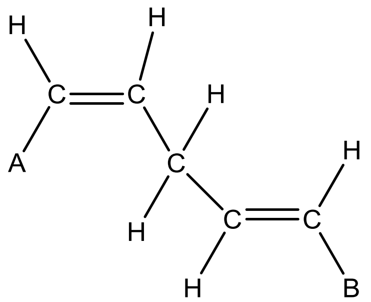
(d) Linoleic acid is an essential fatty acid in human diet.

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

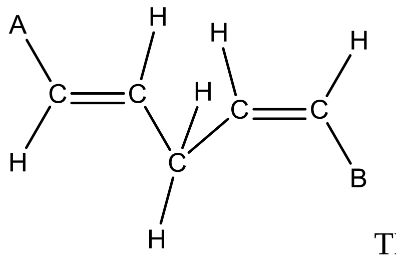
(i) In linoleic acid, both double bonds are in the cis configuration. Representing the formula by the abbreviated structure A-CH=CHCH$_2$CH=CH-B, draw the displayed formulae of linoleic acid and the other possible cis-trans isomers with this structure and label them. **[2]**



CIS- CIS



CIS-TRANS



TRANS-CIS

(ii) Draw the structural formulae of the products obtained when linoleic acid is heated with acidified potassium(VII) manganate. **[2]**

$CH_3(CH_2)_4COOH$
$HOOCCH_2COOH$
$HOOC(CH_2)_7COOH$

(iii) Describe what you will see in the reaction in **(d)(ii)**. **[1]**

Purple solution will be decolourised

[Total: 20 marks]