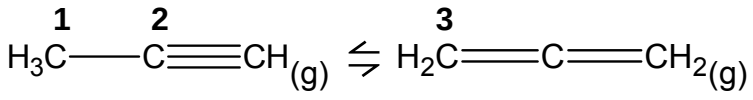
Section A

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

1 (a) Methylacetylene is an alkyne with the chemical formula $CH_3C{\equiv}CH$. It is a component of MAPP gas along with its isomer propadiene, which is commonly used in gas welding. Methylacetylene exists in equilibrium with its isomer, the mixture of methylacetylene and propadiene being called MAPD:



methylacetylene propadiene

(i) State the type of hybridisation, shape and number of sigma and pi bonds about

I C_1 and C_2 of methylacetylene, and

II C_3 of propadiene

in the table below.

Carbon	Hybridisation	Shape	No. of sigma bonds	No. of pi bonds
C_1				
C_2				
C_3				

(ii) When methylacetylene reacts with Br_2 in CCl_4, a compound having the molecular formula of $C_3H_4Br_2$ is formed. Name the type of isomerism shown by the compound and draw all its possible isomers.

Type of isomerism: **.....**

Isomers:

[5]

(b) An experiment was carried out as follows to determine the standard enthalpy change of combustion of methylacetylene contained in the gas cylinder of a gas stove.

A large beaker of water was placed on the stove and heated. The temperature rise was recorded. The cylinder was weighed before and after the experiment to determine the mass of methylacetylene used. This process was known to be only 70% efficient. The following results were obtained.

Mass of methylacetylene before heating = 4.66 g
Mass of methylacetylene after heating = 2.16 g
Mass of water heated = 750 g
Temperature rise = 25.8^{o}C

Assume the heat capacity of water = 4.2 J K^{-1} cm^{-3}

Based on the given data, calculate

(i) the heat absorbed by water;

(ii) the heat given out by methylacetylene during the experiment;

(iii) the enthalpy change of combustion of methylacetylene.

(iv) Hence, use the answer in **(b)(iii)** to calculate the enthalpy change of reaction for the conversion of methylacetylene to propadiene, given that the enthalpy change of combustion of propadiene is -1830 kJ mol^{-1}.

[5]

[Total:10]

2 In nature, chlorine is abundantly found as the chloride ion, a component of the salt that is deposited in the earth or dissolved in the oceans.

The pH of the solutions of chlorides for the elements sodium to phosphorus is given below.

compound	Sodium chloride	Magnesium chloride	Aluminium chloride	Silicon tetrachloride	Phosphorus pentachloride
pH of solution	7	6.5	3	2	2

(a) State the type of structure and bonding present in sodium chloride and silicon tetrachloride.

NaC*l*

.....

$SiCl_4$

.....

[2]

(b) When solid aluminium chloride is heated above 180°C, a vapour is formed which has M_r = 267. When this vapour is heated above 800°C, the vapour has M_r = 133.5.

Draw the displayed formula of the vapour at 180°C to show its bonding.

[1]

(c) Write equations to account for the pH of aqueous solutions of

(i) aluminium chloride

.....

(ii) phosphorus pentachloride

.....

[2]

Chlorine forms various oxides and oxoanions as shown in the following.

Chlorine oxides	Cl_2O	ClO_2	Cl_2O_6	Cl_2O_7
Chlorine oxoacids	$HClO$	$HClO_2$	$HClO_3$	$HClO_4$

(d) Cl_2O_6 exists as singly charged ions in the solid state. The oxidation states of chlorine are +5 and +7 in the cation and anion respectively. Suggest the formulae of the ions and draw the dot-and-cross diagram for the **cation**.

Formulae of the ions: ..... and .....

Dot-and-cross diagram:

[2]

(e) When chlorine gas reacts with water, hypochlorous acid, HC*l*O is formed according to the equation below.

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HClO(aq) + H^+(aq) + Cl^-(aq)$$

At 25^{o}C, 0.10 mole of the chlorine gas is bubbled into 2 dm^3 of distilled water. 55% chlorine remains in the equilibrium solution.

(i) Write an expression for K_c, stating its units.

(ii) Calculate the value of K_c for this reaction.

[3]

[Total: 10]

3 Hydrogen cyanide was first isolated from a blue dye (Prussian blue) which had been known from 1704 and is now known to be a coordination polymer, $Fe_4[Fe^*(CN)_6]_3$.

In the year 2000, 732,552 tonnes of HCN were produced in the US. The most important process is the Andrussov oxidation invented by Leonid Andrussow at IG Farben in which methane and ammonia react in the presence of oxygen and platinum at about 1200 °C:

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$

The energy needed for the reaction is provided by the partial oxidation of methane and ammonia. (1 tonne = 1 000 kg)

HCN is also obtainable from fruits that have a pit, such as cherries, apricots, apples, and bitter almonds, from which almond oil and flavoring are made. Many of these pits contain small amounts of cyanohydrins such as mandelonitrile and amygdalin, which slowly release hydrogen cyanide. An article mentioned that 100 g of crushed apple seeds can yield about 10 mg of HCN.

(a) What is the oxidation number of **(i)** Fe and **(ii)** Fe* in Prussian blue?

(i) **……**

(ii) **……**

(iii) Find the percentage by mass of cyanide in Prussian blue.

(iv) Draw the dot-and-cross diagram for HCN and predict the shape of the molecule.

Dot-and-cross diagram:

Shape: **……**

[3]

(b)(i) Assuming that the amount of HCN produced in US annually is the same, calculate the number of moles of HCN produced in US from 2000-2002.

(ii) What is the volume (in dm^3) of oxygen gas required via the Andrussov oxidation to form the amount of HCN mentioned in **(b)(i)** at r.t.p.?

(iii) What is the role of platinum in the Andrussov oxidation?

……

……

[3]

(c) An apple has an average of 4 seeds and each seed weighs an average of 0.20 g. Find out the mass (in mg) of HCN that can be yielded from seeds of 10 apples.

[1]

(d) (i) HCN gas is a highly poisonous gas that can cause permanent damage to the central nervous system. The toxic level of hydrogen cyanide gas in the air is about 0.001 mg dm^{-3}.

Express the toxic level of hydrogen cyanide gas in the air in terms of mol dm^{-3}.

(ii) How many molecules of HCN are present at this toxic level in 2 dm^3?

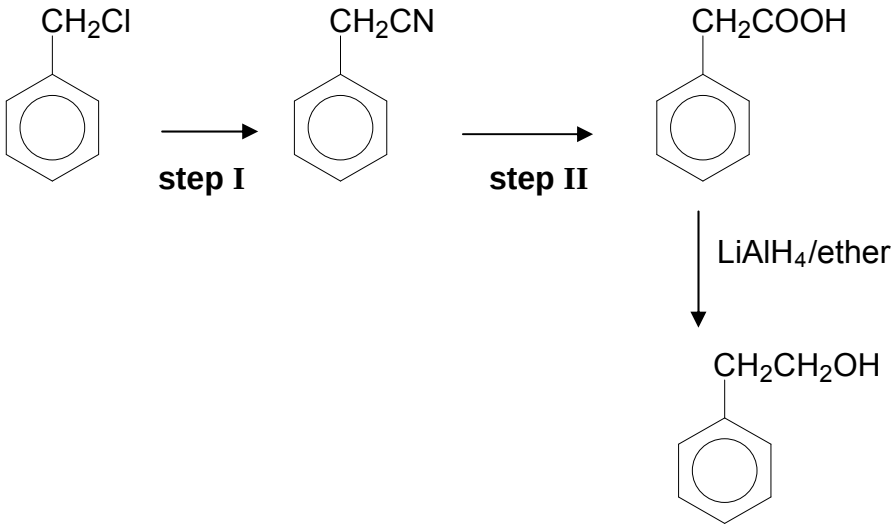
(iii) When it rains, HCN dissolves in water to give an acid solution. If 2 dm^3 of air dissolves in 20 dm^3 of rainwater, find the concentration of H^+ in the acid solution using your answer in **d(i)**.

[Assume HCN dissociates completely in water]

[3]

[Total: 10]

4(a) 2-Phenylethanol occurs naturally in the rose oil, much used in the perfume industry. It can be synthesized from chloromethylbenzene by the following series of reactions.



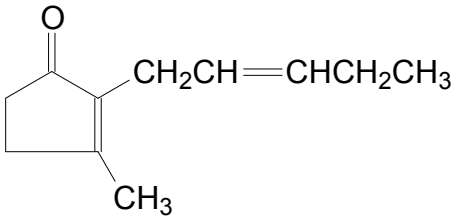
2-phenylethanol

State the reagents, conditions and the type of reaction for steps **I** and **II.**

Step	Reagent	Condition	Type of reaction
I			
II			

[3]

(b) Jasmone is the other active ingredient in jasmine used in the perfume industry. It has the following structure:



(i) How many stereoisomers exist in Jasmone?

……

(ii) Describe a positive test (state reagents, conditions, observations and draw structure of organic product) with each compound that would allow you to distinguish

(I) Jasmone from 2-phenylethanol

Reagents and conditions	Observations	Structure of organic product

(II) 2-phenylethanol from Jasmone

Reagents and conditions	Observations	Structure of organic product

[7]

[Total:10]

Section B

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

5(a) Ethanoic acid, CH_3CO_2H, is a typical weak acid. A solution of ethanoic acid was found to have a pH of 2.8.

(i) Explain the meaning of the term 'weak acid', including an equation in your answer.

(ii) Calculate the hydrogen ion concentration of this acid solution.

(iii) A titration was carried out between the ethanoic acid and 0.10 mol dm^{-3} aqueous sodium hydroxide. State a suitable indicator that could be used to detect the end point and explain the reason for your choice.

[5]

(b) When a solution of ethanoic acid reacts with magnesium metal, hydrogen gas is evolved. The volume of gas evolved for a particular experiment where magnesium was used in excess is given in the table:

Time/ min	0	1	2	3	4	5	6	7	8
Total volume of gas /cm^3	0	23.0	36.5	46.0	51.0	54.5	57.0	58.5	60.0

(i) Write an equation for the reaction between magnesium and ethanoic acid.

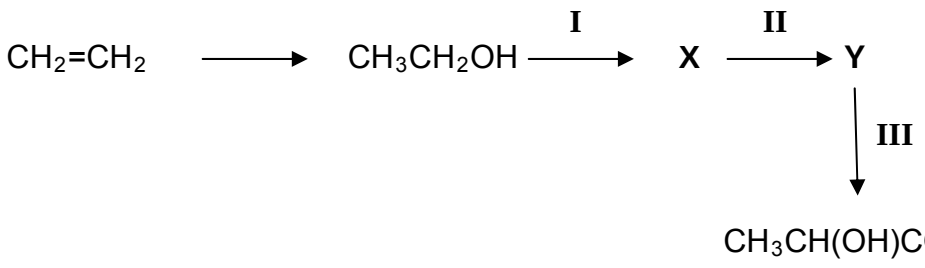
(ii) Plot the experimental results on the graph paper provided.

From the graph, deduce with reasoning, the order of reaction with respect to ethanoic acid. Hence write a rate equation for the reaction.

(iii) A separate experiment using powdered magnesium was used to react with the acid. Explain how this modification could affect the reaction rate.

[8]

(c) The following reaction scheme was proposed to produce 2-hydroxy propanoic acid.



Suggest reagents and conditions for steps **I** to **III**.

Give the structures of the intermediates **X** and **Y**.

If the experiment in **(b)** was repeated using 2-hydroxypropanoic acid,

(i) state the total volume of gas evolved from the reaction;

(ii) explain your answer.

[7]

[Total: 20]

6(a) Sketch a graph of the first ionization energies for sodium to argon and explain the relative values of the first ionization energies of magnesium and aluminium.

[2]

(b) A sample of magnesium oxide is contaminated with some aluminium oxide. By making use of the fact that Period 3 oxides have different acid-base properties, describe a simple method by which a pure sample of magnesium oxide can be obtained. Include an equation for any reaction that is utilized.

[2]

(c) Another Period 3 oxide, sulfur trioxide dissolves in water to form sulfuric acid, H_2SO_4 which can be converted into peroxodisulfuric acid, $H_2S_2O_8$ via the two-step process below, with chlorosulfonic acid, HSO_3Cl, as an intermediate:

$$H_2SO_4 + HCl \rightarrow HSO_3Cl + H_2O$$
$$H_2O_2 + 2HSO_3Cl \rightarrow H_2S_2O_8 + 2HCl$$

(i) The boiling point of H_2SO_4 is 290^{o}C whereas that of HSO_3Cl is 152^{o}C. By comparing the structures of the two compounds, explain the difference in the boiling points.

(ii) Give the displayed formula of the H_2SO_4 molecule, showing the spatial arrangement and estimated bond angle around any one sulfur atom and one oxygen atom.

[5]

(d) Aluminium oxide reacts with chlorine trifluoride, ClF_3, according to the following equation:

$$4ClF_3(g) + 2Al_2O_3(s) \rightarrow 4AlF_3(s) + 2Cl_2(g) + 3O_2(g) \qquad \Delta\overset{\ominus}{H}_r = -1420 \text{ kJ mol}^{-1}$$

(i) Write the equation which corresponds to the standard enthalpy change of formation of chlorine trifluoride.

(ii) Some standard enthalpy changes are given below:

Enthalpy change of formation of $AlF_3(s)$	-1350 kJ mol^{-1}
Enthalpy change of combustion of Al(s)	-840 kJ mol^{-1}

Using the data given in the question, calculate the enthalpy change of formation of chlorine trifluoride.

(iii) Using your answer in **(ii)** and relevant data from the *Data Booklet*, estimate the average bond energy of the C*l*-F bond.

(iv) BrF_3 reacts with aluminium oxide in a way analogous to ClF_3. Assuming that the standard enthalpy change of this reaction is known, explain why a method similar to that used in **(iii)** will yield a less accurate value for the bond energy of the Br–F bond.

[5]

(e) (i) Define the term *lattice energy.*

(ii) State and explain whether the oxide or fluoride ion is smaller.

(iii) Refractories are heat-resistant compounds used to line furnaces. Which compound, magnesium oxide or magnesium fluoride, is more suitable for use as a refractory? Explain your answer.

[6]

[Total: 20]

7 (a) The table below shows the boiling points of some organic compounds.

Name of Compound	Molecular Formula	Boiling Point /°C
Methane	CH_4	-162
Ethane	C_2H_6	-88
Propane	C_3H_8	-42
Butane	C_4H_{10}	0
Cis-but-2-ene	C_4H_8	4
Trans-but-2-ene	C_4H_8	1
Propan-1-ol	$CH_3CH_2CH_2OH$	97
Propanal	CH_3CH_2CHO	49
Propanone	CH_3COCH_3	56

(i) Explain the difference between the boiling points of *cis*-but-2-ene and *trans*-but-2-ene.

(ii) Explain why the boiling point of propan-1-ol is higher than that of propanal and propanone.

(iii) If the intermolecular bonding in propan-1-ol is the same as that in the alkanes, predict a value for its boiling point. Explain your answer.

(iv) As compared to the alkanes, alcohols are more soluble in water. Draw a diagram to show the interaction between propan-1-ol molecules and water molecules.

[7]

(b) 0.10 mole of an organic compound **A**, $C_xH_yO_z$ gives 0.40 mole of carbon dioxide and 0.40 mole of water vapour upon complete combustion. 8.80 g of **A** when vapourised, was found to occupy 2.40 dm^3 at room temperature and pressure.

Compound **A** does **not** react with aqueous sodium hydroxide. However, it forms a pale yellow precipitate when warmed with alkaline aqueous iodine. **A** reacts with $SOCl_2$ and liberates gaseous products. A silver mirror is observed when **A** is warmed with Tollen's reagent.

Compound **B**, an isomer of **A**, is neutral to litmus. On treatment with hot aqueous sodium hydroxide, **B** yields **C**, $C_2H_3O_2Na$ and **D**, C_2H_6O.

(i) Determine the molecular formula of **A**.

(ii) Deduce, with reasoning, the structures of **A**, **B**, **C** and **D**.
[Chemical equations are **not** required.]

[10]

(c) Suggest reagents and conditions for converting butan-1-ol to 2-chlorobutane. Draw the structure of the intermediate product.

[3]

[Total: 20]