Answer any **four** questions.

1 (a) Samples of 2-bromo-2-methylpropane were dissolved in dilute aqueous ethanol (80% ethanol and 20% water by volume) and reacted with sodium hydroxide solution. Several experiments were carried out at constant temperature. The initial rate of reaction was determined in each case.

Expt	$[(CH_3)_3CBr]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.020	0.010	20.2
2	0.020	0.020	20.2
3	0.040	0.030	40.4

Calculate a value for the rate constant. Hence write the rate equation for the reaction.

[3]

(b) The hydrolysis of 2-bromopropane is now investigated. Samples were dissolved in dilute aqueous ethanol (80% ethanol and 20% water by volume) and reacted with sodium hydroxide solution. The rate equation is found to be as follows:

$$\text{Rate} = 0.24 \times 10^{-5} [CH(CH_3)_2Br] + 4.7 \times 10^{-5} [CH(CH_3)_2Br] [OH^-]$$

(i) The rate equation obtained indicates that the hydrolysis of 2-bromopropane exhibits a mixture of both first order and second order kinetics. Suggest why this may be so.

[2]

(ii) By deriving an expression in terms of $[OH^-]$, show that the % rate due to S_N2 is $\frac{4.7[OH^-]}{4.7[OH^-] + 0.24} \times 100\%$.

[1]

(iii) Using the expression derived from **(b)(ii)**, calculate the % rate due to S_N2 for various $[OH^-]$ of 0.01M, 0.1M and 1.0M.

[1]

(iv) In light of your answer to **(b)(iii)**, state how the % rate due to S_N2 depends on the concentration of $[OH^-]$ and explain why it varies in that manner.

[2]

(v) By comparing the magnitude of the two rate constants in the rate equation given in **(b)**, comment on the ease of hydrolysis by the two different pathways.

The Arrhenius Equation is given as follows:

$$k = A\, e^{-Ea / RT}$$

[2]

(vi) Draw a labelled Maxwell-Boltzmann Curve for this reaction to illustrate the distribution of energy. Based on your answer to **(b)(v)**, indicate the activation energies clearly on the diagram for the two different reaction pathways.

[3]

(vii) On the same axes, draw the energy profile illustrating both the S_N1 kinetics and the S_N2 kinetics components observed for this reaction. Indicate the activation energies clearly on the diagram, for the two reaction pathways.

[2]

(viii) Explain how the rate constant will change if $CH(CH_3)_2Cl$ is used instead of $CH(CH_3)_2Br$.

[2]

(ix) Draw the structures of two possible organic by-products that may be formed in this reaction, other than $CH(CH_3)_2(OH)$. Briefly account for their formations.

[2]

[Total: 20 marks]

2 Oxalic acid is an organic compound with the formula $H_2C_2O_4$. This colourless solid is a dicarboxylic acid. In terms of acid strength, it is about 3,000 times stronger than acetic acid. Its conjugate base, known as oxalate ($C_2O_4^{2-}$), is a reducing agent as well as a chelating agent for metal cations.

Oxalic acid dissociates in water according to the following equations

I: $HOOC\text{-}COOH + H_2O \rightleftharpoons HOOC\text{-}COO^- + H_3O^+$ $\quad K_{a1} = 5.6 \times 10^{-2}$ mol dm^{-3}

II: $HOOC\text{-}COO^- + H_2O \rightleftharpoons {}^-OOC\text{-}COO^- + H_3O^+$ $\quad K_{a2} = 5.4 \times 10^{-5}$ mol dm^{-3}

(a) (i) Explain why the value of Ka_1 is larger than Ka_2.

[1]

(ii) Write expressions for the acid dissociation constants for equation **I** and **II** above.

[2]

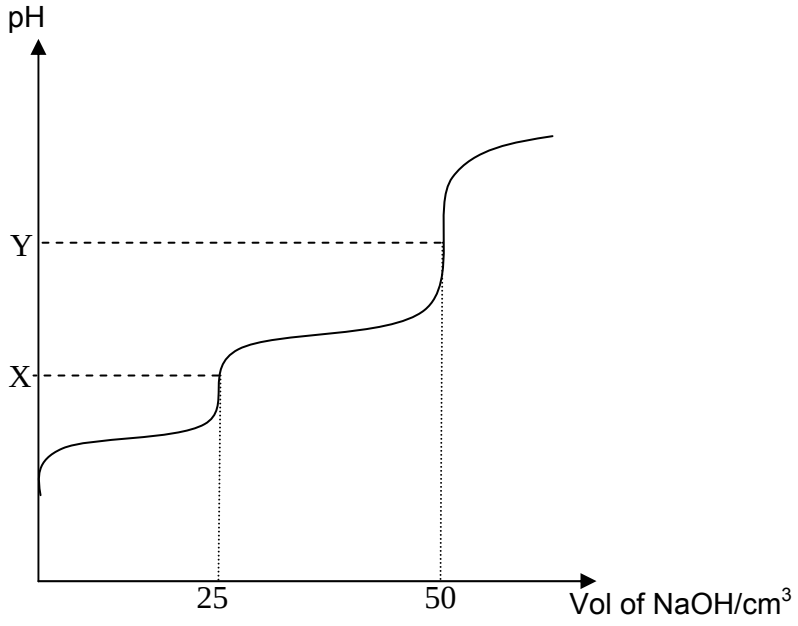
(b) (i) The neutralisation between oxalic acid and sodium hydroxide corresponds to the two equations given:

$HOOC\text{-}COOH + NaOH \rightarrow HOOC\text{-}COONa + H_2O$ **step 1**

$HOOC\text{-}COONa + NaOH \rightarrow NaOOC\text{-}COONa + H_2O$ **step 2**

A 25 cm^3 sample of 0.100 mol dm^{-3} of oxalic acid was titrated with 0.100 mol dm^{-3} of sodium hydroxide.

The titration curve for the above titration was given below.



At the first equivalent point, **X**, the species formed is $HOOC\text{-}COO^-(aq)$, which is both an acid and a base where the relevant equilibriums are:

$$HOOC\text{-}COO^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + (COO)_2^{2-}(aq)$$
$$HOOC\text{-}COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + (COOH)_2(aq)$$

It can be shown that in such an instance the $[H_3O^+]$ at the first equivalent point, **X**, can be given by expression,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

Using the expression, determine the pH value at point **X**.

[1]

(ii) Calculate the pH value at the second equivalent point, **Y**, given that the $[OH^-]$ can be assumed to be entirely due to the hydrolysis:

$$^-OOC\text{-}COO^- + H_2O \rightleftharpoons HOOC\text{-}COO^- + OH^-$$

[3]

(c) The concentration of oxalic acid in a solution can be determined by an acid-base titration. State another way by which the concentration can be determined volumetrically.

[1]

(d) Oxalate, the salt from oxalic acid, is able to combine chemically with certain metals commonly found in the human body, it is also able to bond chemically, behaving as **bidentate** chelating agents, to transition elements, such as iron to form **complex ion**. A **chelating agent** is a **ligand** that is attached to a central metal ion by bonds from two or more donor atoms.

$$[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6H_2O \quad K_{stab} = 5.00 \times 10^4$$

(i) What do you understand by the term "**bidentate" ligand**.

[1]

(ii) Suggest a reason why the stability constant of the above is greater than 1.

[1]

(iii) Draw the structure of the complex ion, $[Fe(C_2O_4)_3]^{3-}$.
State the type of bonds formed between the ligands and the metal ion.
Hence suggest the shape for this complex.

[3]

(e) Oxalic acid was one of the products formed when an aromatic organic compound, **A,** with molecular formula $C_{10}H_{10}O_2$ undergoes oxidation with acidified manganate(VII) to form another organic product, **B**, with the molecular formula $C_8H_8O_2$. No other organic compound was formed in the oxidation. Compound **B** reacts readily with 2 moles of $Br_2(aq)$ to form compound **E**, $C_8H_6O_2Br_2$. Compounds **A** and **B** are both soluble in NaOH and both **A** and **B** reacts with 2,4 - DNPH. Compound **A** reacts with acidified dichromate to give an acid, **C**, $C_{10}H_{10}O_3$. Compound **C** reacts with $SOCl_2$ to form a sweet-smelling compound **D**, $C_{10}H_8O_2$. Deduce the structures of **A, B, C, D** and **E.** Explain your deductions

[7]

[Total: 20 marks]

3 The *lac* repressor is a DNA-binding protein which inhibits formation of proteins involved in the metabolism of lactose in bacteria. It is active in the absence of lactose, ensuring that the bacterium only invests energy metabolism of lactose when lactose is present. When lactose becomes available, it is converted into allolactose, which inhibits the *lac* repressor's DNA binding ability.
Structurally, the *lac* repressor is a homotetramer made up of four identical polypeptides, each consisting of 347 amino acid residues.

(a) (i) State the highest level of protein structure in the *lac* repressor.

(ii) One of the most common features in the secondary structure of proteins is the α-helix. Draw a diagram of the α-helix, showing the bonding which maintains the structure.

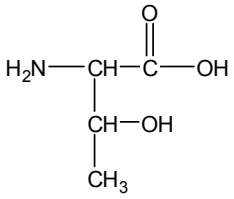
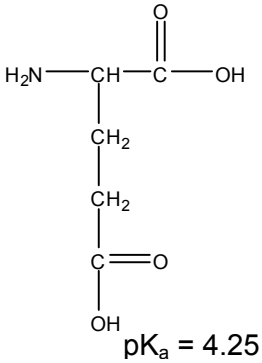
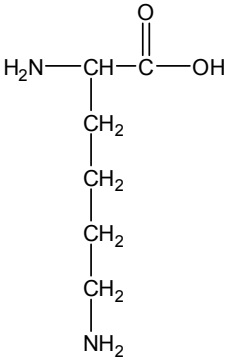
[2]

(b) (i) An 18 residue section from the *lac* repressor was digested using two types of enzymes. The enzymatic hydrolysis gave rise to these fragments.

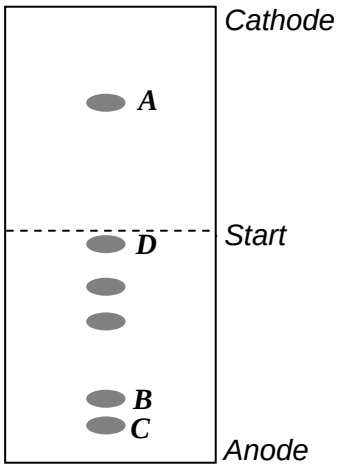
Enzyme 1	Enzyme 2
Tyr-Trp-Leu-Val-Arg Glu-Glu-Met-Lys Val-Asp Asp-Asp-Phe Gly-Trp-Leu-Ala	Gly-Trp-Leu-Ala-Glu Lys-Tyr-Trp-Leu Val-Asp-Asp Glu-Met Val-Arg Asp-Phe

Suggest the primary sequence of this 18 residue polypeptide.

(ii) Another segment of tripeptide, Thr-Glu-Lys, was subjected briefly to acidic hydrolysis which produced individual amino acids as well as various peptides due to partial hydrolysis. The resulting mixture buffered at pH 8 was separated in an electric field using electrophoresis.

Amino acid	$pK_a = 2.09$  $M_r = 131$	$pK_a = 2.19$ $pK_a = 4.25$  $M_r = 147$	$pK_a = 2.18$  $M_r = 146$
Abbreviation	Thr	Glu	Lys
pI	5.60	3.22	9.74

Match each of the three amino acids to the spots **A**, **B** and **C**.



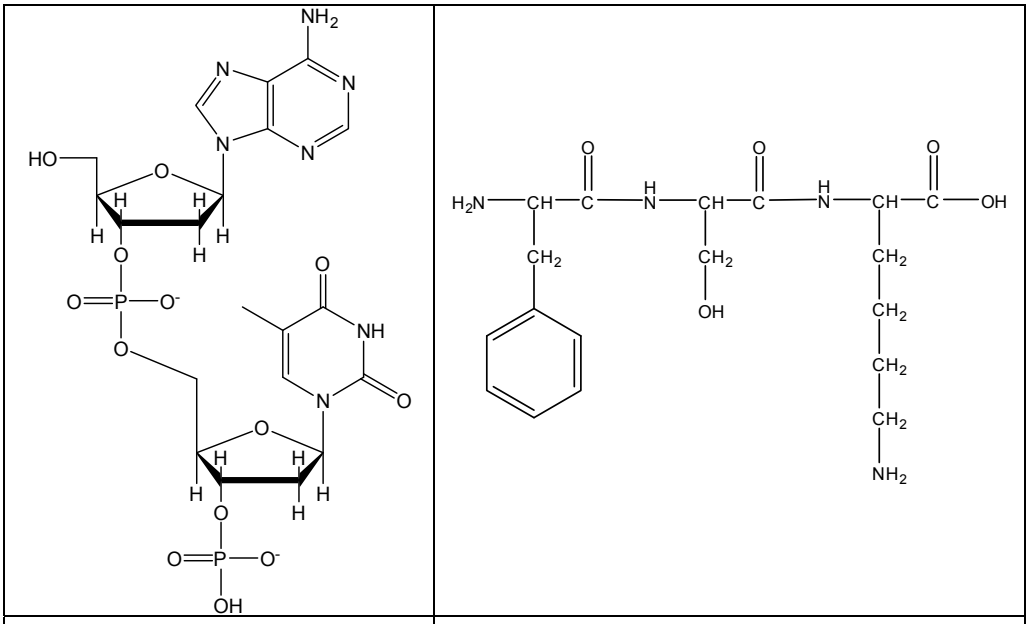
(iii) Given that longer peptide strands show greater resistance when migrating through the electrophoresis plate, suggest a structure of the substance at spot D when the electrophoresis was buffered at pH 8.

(iv) Threonine (Thr) can be used as a buffer at pH 7. Show with the aid of equations how it serves as a buffer at this pH.

[7]

(c) *lac* repressor can be purified using affinity chromatography. In this technique, the natural substrate of the *lac* repressor, a specific DNA sequence, is covalently attached to a chromatographic support.
When a mixture of proteins is poured into the chromatographic column, *lac* repressor proteins bind specifically to its natural substrate, while other proteins are washed through. This step is pH sensitive and a suitable buffer is used to maintain optimal binding pH.

(i) Suggest ***two*** types of bonding that could take place between the following amino acid side chains of the *lac* repressor and DNA nucleotides.



DNA sequence	Section of peptide sequence from *lac* repressor

(c) After washing away impurities, the target molecule is eluted (i.e. released from the chromatographic column) using one of a variety of methods, such as changing the pH within the chromatographic column. This weakens the protein binding and causes pure *lac* repressor protein to be washed through.

(ii) For a protein that binds fully to the covalently bonded substrate, determine the pH for 70% of the protein to be eluted given that

$$\text{Protein-Substrate complex (aq)} + H^+\text{ (aq)} \rightleftharpoons \text{Protein-}H^+\text{ (aq)} + \text{Substrate (s)}$$

$$K_b = 8.81 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$$

(iii) When pH in the chromatographic column is adjusted to elute the purified protein, care must be taken to maintain very mild pH conditions.

Suggest how the protein structure is affected when pH for elution is too high (e.g. pH 12) and explain your answer using lysine (Lys) and glutamic acid (Glu).

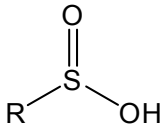
(iv) Uncoiling of the protein structure is favoured when temperature is higher than physiological conditions. With the aid of the equation,

$$\Delta G = \Delta H - T\Delta S$$

suggest why this process is favoured at higher temperature such as 70 °C.

[8]

(d)



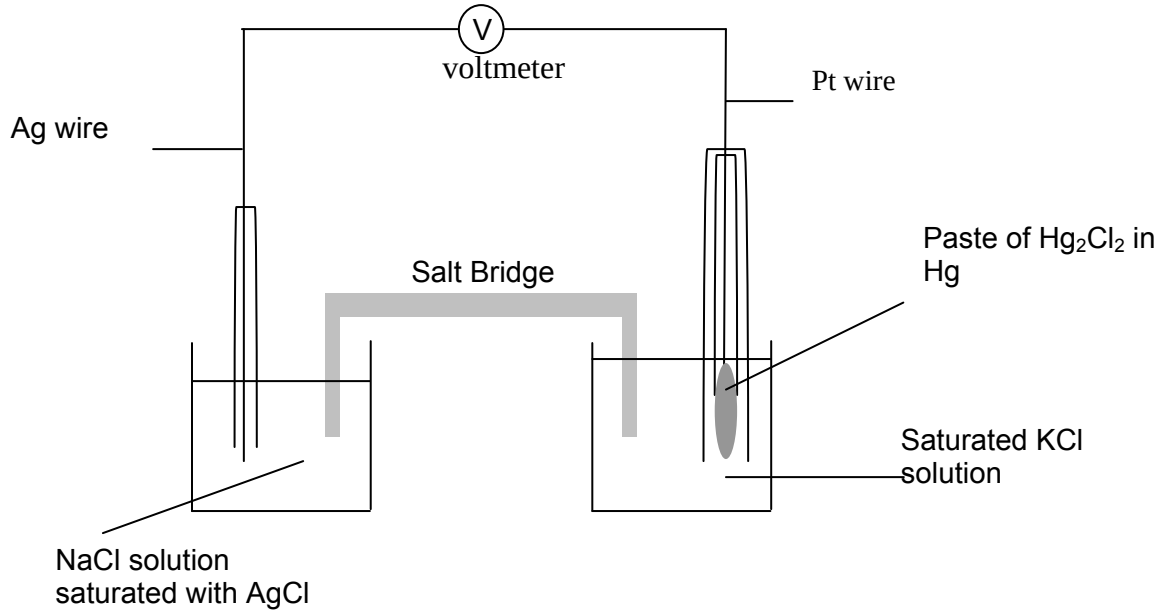
Sulfinic acids are reactive species with structure similar to carboxylic acid. Unlike carboxylic acids, the analogous sulfinic acids are chiral.

Using VSEPR theory, deduce the shape of the molecule using and draw the pair of optical isomers.

[3]

[Total: 20 marks]

4 A chemist designs an ion-specific probe for measuring $[Ag^+]$ in a NaCl solution saturated with AgCl using the following set- up.



(a) (i) Given the following standard half reactions:

$$Hg_2Cl_2(s) + 2e \rightleftharpoons 2Hg(s) + 2Cl^-(aq) \qquad E^{ø}_{red} = +0.24\ V$$

$$Ag^+(aq) + e \rightleftharpoons Ag(s) \qquad E^{ø}_{red} = +0.80\ V$$

Obtain an overall balanced equation, including state symbols for the cell above and state the direction of the **flow of electron** in the cell.

[2]

(ii) An engineer wishes to use the probe to analyse an ore sample. After pretreating the sample, the chemist measured the cell voltage, E_{cell} as 0.53V.

The Nernst equation can be used to measure the concentration of silver ions using the probe,

$$E_{cell} = E^{ø}_{cell} - \frac{0.0592}{n} \log_{10} K$$

where n is the no of moles of electrons transferred in the overall reaction and K is the equilibrium constant for the overall equation in **(a)(i)**.

Assuming the concentration of Cl^- is so high that it is essentially constant, use the Nernst equation to calculate the concentration of silver ions in the ore sample

[3]

(iii) Given that,

$$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^-(aq) \quad E^{\ominus}_{red} = +0.22\ V$$

Using the half equation above and any other relevant data from the Data Booklet, derive the $E^{\ominus}_{cell}$ for the overall reaction: **$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$** and use the equation given in **(a)(ii)**, calculate a value of the K_{sp} for silver chloride **at equilibrium**, if E_{cell} of any process at equilibrium is 0V.

[3]

(b) **(i)** To prepare the saturated solution of AgCl and NaCl. AgCl is added to a 200 cm^3 solution of NaCl of concentration of 1×10^{-3} mol dm^{-3}. Using the K_{sp} value obtained in **(a)(iii)**, predict the maximum mass of AgCl to be added to obtain a saturated solution. If you had not been able to obtain a value for the K_{sp} in **(a)(iii)**, assume a value of 1.59×10^{-10} mol^2 dm^{-6}.

[2]

(ii) The concentration of chloride ions from silver chloride in **(b)(i)** is less than the square root of the K_{sp} value of silver chloride. Explain why this is so.

[1]

(iii) Suggest why when aqueous sodium thiosulfate was added to the resulting solution in **(b)(i)**, more silver chloride was able to dissolve.

[3]

(c) In 1999, researchers in Israel reported a new type of alkaline battery, called the "*super iron*" battery. This battery used the same anode reaction as an ordinary alkaline battery.

The overall equation for the cell was found to be:

$$2\ FeO_4^{2-}(aq) + 8H_2O(l) + 3\ Zn(s) \rightarrow 3Zn(OH)_2(s) + 2\ Fe(OH)_3(s) + 4\ OH^-(aq)$$

(i) Construct the half-equations, with state symbols, for each electrode reaction in **alkaline** conditions.

[2]

(ii) A "super-iron" battery should last longer than an ordinary alkaline battery of the same size and weight.

Calculate the quantity of charge released by the reduction of 10.0 g of K_2FeO_4 to $Fe(OH)_3$.

[3]

(iii) Suggest a reason why the "super-iron" battery can last longer, given that for a normal alkaline battery, the reaction at the cathode is:

$$2MnO_2(s) + 2NH_4^+(aq) + 2e \rightarrow 2NH_3(aq) + 2MnO(OH)\ (s)$$

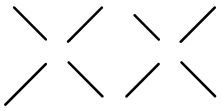
[1]

[Total: 20 marks]

5 (a) Boron is used in the manufacture of boron steel and boron carbide is used for shielding in nuclear reactors and as control rods for nuclear reactors. Boron reacts with hydrogen to form a series of hydrides. Upon thermal decomposition, the simplest of the hydrides when analysed, is found to comprise 78.3% B and 21.7% H.
Find the empirical formula of this hydride.

[1]

(b) This hydride actually exists in the form of a gaseous dimer (diborane). This dimer is 'unusual' in the way some of the hydrogen atoms are involved in bonding. The structure of diborane is similar to Al_2Cl_6 as shown below.



(i) Unlike Al_2Cl_6, what do you think is 'unusual' about this dimer?

(ii) Using the data given below and any relevant data where applicable from the Data Booklet, construct an energy cycle to calculate the bond energy for the bridging H_b – B bond.

$\Delta H_f B_2H_6(g) = +36.4$ kJ mol^{-1}
ΔH atomisation B(s) = +563 kJ mol^{-1}
Bond energy of B – H_a = +340 kJ mol^{-1}

(iii) In the light of your answer to **(b)(ii)**, do you then expect the B – H_a bonds to be of the same length as that of B – H_b bond?
Explain any difference that is expected.

(iv) Despite the unusual characteristics, BH_3 tends to exist as a dimer instead of a monomer. Given the following data to calculate the ΔG^o for the dimerisation, show that B_2H_6 is energetically more favourable than BH_3.

$\Delta H_f BH_3(g) = +89.2$ kJ mol^{-1}
S^o $BH_3(g) = 188.2$ J mol^{-1} K^{-1}
S^o $B_2H_6(g) = 232.1$ J mol^{-1} K^{-1}

(v) Would you expect AlH_3 to be able to exist in a form similar to diborane? Explain.

[8]

(c) When diborane is reacted with ammonia, a nucleophilic substitution reaction occurs resulting in a compound, $B_2H_{12}N_2$ which is found to have electrical conductivity in the molten state. Given that one mol of diborane reacted with 2 moles of ammonia, suggest a possible structural formula for this compound.

[1]

(d) Diborane is a powerful electrophilic reducing agent and is used in the reduction of certain functional groups. It attacks sites with a high electron density such as N atom in cyanides and nitriles and O atom in carbonyl compounds. However it is a highly reactive gas which catches fire spontaneously in air. Thus its direct use is restricted. Hence many organic syntheses (involving reduction) make use of the safer solid hydrides as reducing agents. A typical example is sodium borohydride, $NaBH_4$, which is commonly used to reduce carbonyl compounds. However, it cannot be used in reduction of alkenes to alkanes. Suggest a reason for this.

[1]

(e) In practice, R-X (where X = Cl or Br) can react with ammonia to form an alkylammonium salt where the amine formed in the reaction mixture will react with HX. An alkali has to be added to the mixture to liberate the free amine. The reaction scheme for the formation of free amine is as follows:

$$R\text{-}X + NH_3 \xrightarrow[\text{heat}]{\text{alcohol, sealed tube}} R\text{-}NH_3^+ X^- \xrightarrow{NaOH\ (aq)} R\text{-}NH_2 + H_2O + NaX$$

Consider the three organic halogen compounds, **A**, **B** and **C** shown below

CH_3CH_2Cl	$CH_2{=}CHCl$	$CH_2{=}CHCH_2Cl$
A	**B**	**C**

(i) State the type of hybridization of the carbon atom of the C-X bond for all the three halogen compounds.

(ii) Separate samples of **A**, **B** and **C** were warmed initially with aqueous ethanolic sliver nitrate and left to stand. A white precipitate was expected to appear in one or more of the samples.

The difference in reactivity between the different organic halogen compounds and the nucleophile can be owed to the different strength of the C-X bond. With reference to your answer to (i), which sample will yield a precipitate and why?

(iii) **A** can be converted to a primary amine by reacting it with ammonia is in a sealed tube. However for a good yield of the amine, **A** must be used in limiting amount. However when ethanoyl chloride is reacted with ammonia to form the primary amide, a good yield is obtained even if the ethanoyl chloride is in excess. Explain.

[5]

(f) Explain the following observations:

(i) Nitration of methylbenzene gives approximately equal proportions of the 1,2- and 1,4-isomers, but nitration under the same conditions of the compound $C_6H_5C(CH_3)_3$ gives 90% of the 1,4-isomer.

(ii) HCl (g) will add to the C=C bond in $CH_2{=}CH_2$ but not to the C=O bond in CH_3COCH_3.

[4]

[Total: 20 marks]