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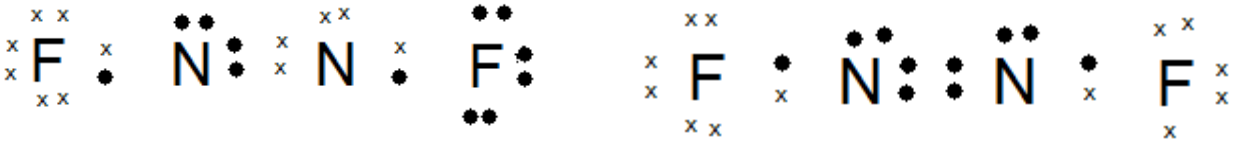
Solution

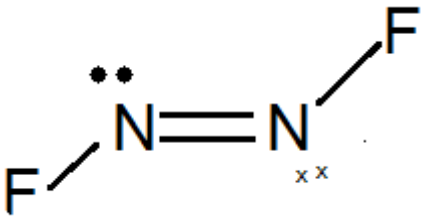
1a) (i)



or

Shape about N: Bent

(ii) Type of isomerism: cis-trans or geometric isomerism



More stable isomer

1b) (i) Dynamic equilibrium refers to an equilibrium reaction when the rate of forward is equal to the rate of backward reaction.

$K_p = \dfrac{P_{N_2F_2}}{(P_{N_2})(P_{F_2})}$ Units: Pa^{-1} or atm^{-1}

(ii) $pV = nRT$

$pV = \dfrac{m}{M}RT$

$M = \dfrac{mRT}{pV} = \dfrac{0.578 \times 8.31 \times 500}{1.12 \times 10^5 \times 500 \times 10^6} = 42.9\ gmol^{-1}$

	N_2	F_2	N_2F_2
Initial n/mol	2	1	0
Change of n/mol	-x	-x	x
Equilibrium n/mol	2-x	1-x	x

Total number of moles = (2-x) + (1-x) + x = 3-x

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(Note: sum of mole fraction x Mr for each gases = average Mr)

$$\frac{2-x}{3-x}(28)+\frac{1-x}{3-x}(38)+\frac{x}{3-x}(66)=42.9$$

x = 0.576mol

Mole fraction of N_2F_2 = $\frac{\text{moles of } N_2F_2}{\text{total moles of gases}}=\frac{x}{3-x}=\frac{0.576}{3-0.576}=0.237$

(ii) Partial pressure of N_2F_2 = mole fraction of N_2F_2 x total pressure

= 0.237 x 1.12 x 10^5

= 26500 Pa

(iii) ΔS is negative. There is a decrease in number of moles of gas in the reaction and the system becomes more ordered.

(iii) $\Delta G=\Delta H-T\Delta S$. Since ΔS is negative and T is always positive, therefore, $-T\Delta S$ is positive. In order for ΔG to be negative, ΔH must be negative and have a magnitude greater than $T\Delta S$.

1 c) **A** = P_2O_4

	P	O
	49%	51%
$\frac{mass\%}{Ar}$	$\frac{49}{31.1}=1.57$	$\frac{51}{16.0}=3.18$
Simplest ratio	1	2

Empirical formula of **A** = PO_2 [1]

$P_2O_4 + 3H_2O \rightarrow H_3PO_3 + H_3PO_4$

A

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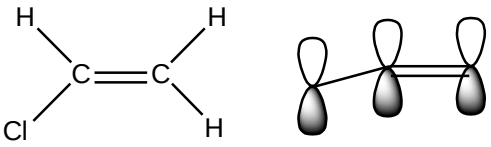
Solution

1 d) (i)



In chloroethene, as Cl is adjacent to the C=C bond, *p-orbital of Cl can overlap with the π electron cloud of C=C bond*. Hence **lone pair of electrons on Cl is delocalised into the π electron cloud of C=C bond**, strengthening C–Cl bond (*partial double bond character*).

Thus C–Cl bond in chloroethene cannot be cleaved, no free Cl^- ions formed, hence AgCl ppt is not produced.

1 d) (ii) Greater reactivity of the acyl chloride C–Cl bond in C_6H_5COCl/ the acyl chloride is more reactive because

- the acyl carbon atom is bonded to 2 electronegative atoms, Cl and O which makes the carbon atom more electron-deficient/more partial positive. OR
- the electron withdrawing C=O bond makes the carbon atom bonded to Cl more electron-deficient/more partial positive.

Hence the δ+ C is more susceptible to nucleophilic attack by water molecules. C–Cl bond breaks readily to give Cl^- ions which gives AgCl, white ppt with $AgNO_3$(aq).

2 a) Reducing agent: H_2O
Relevant data required:

Reduction:	$MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$	$E^o_{red} = +1.67V$
Oxidation:	$2H_2O \rightarrow O_2 + 4H^+ + 4e$	$E^o_{oxid} = -1.23V$
Overall	$4MnO_4^- + 4H^+ + 4OH^- \rightarrow 4MnO_2 + 2H_2O + 3O_2 + 4OH^-$	$E^o_{cell} = +0.44V$

i.e. $4MnO_4^- + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4OH^-$ is a spontaneous rxn.

2 b) As SO_3^{2-} reacts with MnO_4^- in a 1:1 ratio and SO_3^{2-} can be oxidised to SO_4^{2-}, thus $SO_3^{2-} \equiv MnO_4^- \equiv 2e$ and a likely formula for the manganese species is such that Mn is in the +5 oxidation state.

Relevant eqn: $SO_3^{2-} + MnO_4^- \rightarrow SO_4^{2-} + MnO_3^-$
OR $SO_3^{2-} + MnO_4^- + 2OH^- \rightarrow SO_4^{2-} + MnO_4^{3-} + H_2O$

2 c) Reaction between 2 negatively charged ions, $C_2O_4^{2-}$ and MnO_4^-, involves high activation energy $\Rightarrow$ reaction rate is slow at room temp.
Warming/heating is required to hasten the reaction rate as at a higher temp, more molecules will have acquired energy greater than or equal to the activation energy.

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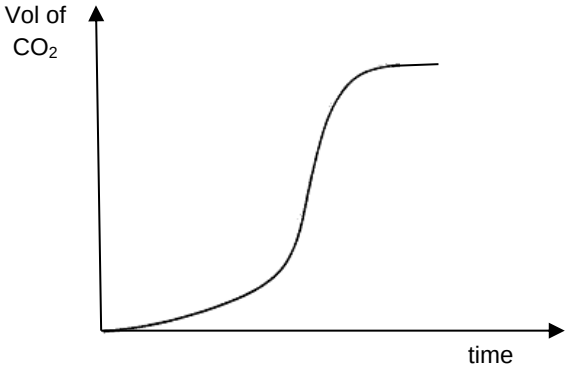
2 d) (i) Plot a graph of $[MnO_4^-]$ against time.

Determine 2 half-life from the graph and show that they have the same value or approximately the same ($t_{1/2} \approx 15s$).
Rate = $k[MnO_4^-]$

2 d) (ii) Rate of consumption of $C_2O_4^{2-}$ = 5/2 x Rate of consumption of MnO_4^-
= 3.0×10^{-4} mol dm^{-3} s^{-1}

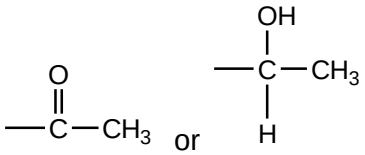
2 d) (iii) Homogeneous catalyst

2 d) (iv)



- At the beginning of the reaction, the production of CO_2 is slow and low because fruitful collision of negatively charged MnO_4^- and $C_2O_4^{2-}$ ions is difficult.
- Once a certain amount of Mn^{2+} has been formed, the production of CO_2 increases rapidly because Mn^{2+} acts as the catalyst for the reaction (autocatalyst).
- Vol of CO_2 remains constant after some time even though there is an adequate supply of catalyst as the reaction has reached completion.

2 e)

Observations	Deductions
C gives yellow ppt with alkaline aq I_2.	• **C** contains either methyl carbonyl group  or structure.
C has no reaction with Tollen's reagent.	• **C** is not an aldehyde.
C ($C_6H_{10}O_2$) $\xrightarrow{hot\ H^+ / KMnO_4}$ **D** ($C_4H_6O_3$) only product	• **C** is oxidized (vigorous oxidation/ oxidative cleavage of C=C bond). • **D** contains a carboxylic acid group

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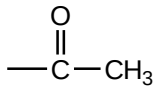
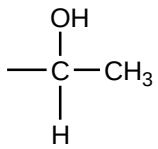
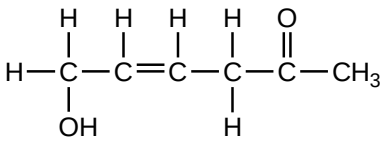
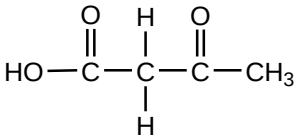
Solution

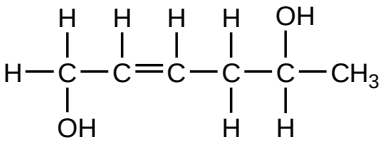
	(increase in no. of O atoms) • **C** loses 2 carbon atoms as CO_2 gas. • i.e. oxidative cleavage of C=C bond resulted in ethanedioic acid which is further oxidized to CO_2 / C=C bond is between C2 and C3.
C ($C_6H_{10}O_2$) $\xrightarrow{NaBH_4}$ **E** ($C_6H_{12}O_2$)	• **C** is reduced. • **C** contains an alcohol group and a methyl carbonyl group  which is reduced to  in **E**.



C



D



E

3 a) (i) CI_2(g), or CI_2 in CCI_4, room temperature, dark

Electrophilic addition

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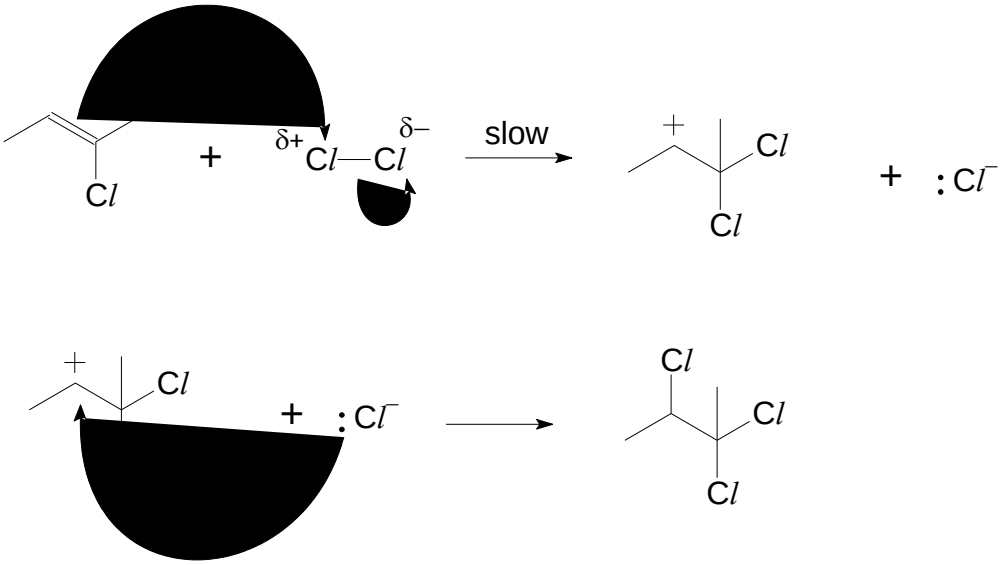
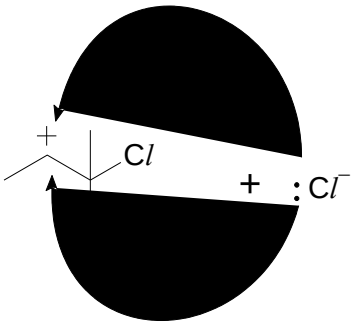
Solution



Note:

- The type of mechanism reaction must be stated.
- The mechanism arrows must be shown in the equation to illustrate the movement of electrons.
- Lone pair on the chloride ion must be clearly shown.
- Slow step and the partial charges on chlorine must be indicated in the mechanism

3 a) (ii) The geometry about the positive charge carbon atom of the carbocation from the slow step is **trigonal planar**.



Hence, :Cl^- has **equal chances of attacking from both above and below the plane**, to produce **equal amount of the 2 enantiomers**, resulting an **racemic mixture** whereby the **optical activity of the two enantiomers cancel out each other completely**. Thus, it is not optically active.

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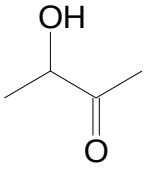
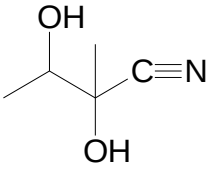
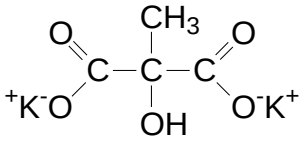
Solution

3 a) (iii) **Q** **R**

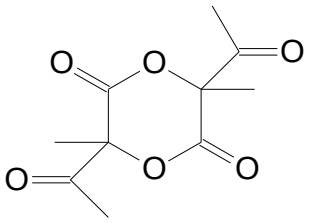




3 a) (iv) CHI_3



3 b) Concentrated sulfuric acid acts as catalyst (Hint: limited amount of conc H_2SO_4).



3 c) (i) The standard enthalpy change of formation of HI(g) is the **heat absorbed** when **1 mole of HI(g)** is formed from $H_2(g)$ and $I_2(s)$ (or constituent elements in their standard state) under standard conditions of 1atm at 298K.

or $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(s) \rightarrow HI(g)$ $\quad \Delta H>0$

3 c) (ii) As ΔH_f of H-X becomes less exothermic from HCl(g) to HBr(g) to HI(g), the reaction does not occur as readily since the formation of HX is less energetically favourable. Thus, reactivity of chlorine, bromine and iodine with hydrogen decreases.

Or

From chlorine to bromine to iodine, the halogen exists as gas to liquid to solid. Thus, more energy is required to overcome the Van der Waals force from chlorine to bromine to iodine to form HX, resulting ΔH_f of H-X to become more endothermic. Therefore, the reaction does not occur as readily and thus, reactivity of chlorine, bromine and iodine with hydrogen decreases.

Or

As H-X bond strength decreases from H-C*l* to H-Br to H-I, the stability of HX decrease with less heat evolved. Hence, ΔH_f of H-X becomes more endothermic.and the reaction occurs less readily. Thus, reactivity of chlorine, bromine and iodine with hydrogen decreases.

3 c) (iii) **Volatility** of hydrogen halide, HX**, decreases from HCl, to HBr to HI**. As the **electron cloud size of halogen atom increases from Cl to Br to I**, there is **greater ease of distortion/polarization of the electron cloud of HX**. Thus, **more energy is needed to overcome the stronger td-id interaction** from HCl to HBr and HI to form vapour.

3d) K_{sp} value of $PbBr_2 = 6.6 \times 10^{-6}$

K_{sp} value of $AgBr = 5.4 \times 10^{-13}$

At the point which $PbBr_2$ just begins to precipitate:

Ionic Product of $PbBr_2 = K_{sp}$ of $PbBr_2$

$\therefore \quad [Pb^{2+}][Br^-]^2 = 6.6 \times 10^{-6}$

$[1 \times 10^{-2}][Br^-]^2 = 6.6 \times 10^{-6}$

$[Br^-] = (6.6 \times 10^{-6}/1 \times 10^{-2})^{1/2}$

$= 0.02569 \text{ mol dm}^{-3}$

Given $[Br^-] = 0.02569 \text{ mol dm}^{-3}$ at the point which $PbBr_2$ begins to precipitate:

$[Ag^+][Br^-] = 5.4 \times 10^{-13}$

$[Ag^+][0.02569] = 5.4 \times 10^{-13}$

$[Ag^+] = (5.4 \times 10^{-13}/0.02569)$

$= 2.102 \times 10^{-11} \text{ mol dm}^{-3}$

$[Ag^+]$ in the resultant saturated solution $= 2.102 \times 10^{-11} \text{ mol dm}^{-3}$

$[Ag^+]$ precipitated $= 1 \times 10^{-9} - 2.102 \times 10^{-11}$

$= 9.790 \times 10^{-10} \text{ mol dm}^{-3}$

% of Ag^+ precipitated $= [(9.790 \times 10^{-10})/(1 \times 10^{-9})] \times 100$

$= 97.9\%$

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Solution

4 a) (i) $MgCO_3$ (s) $\rightarrow$ MgO (s) + CO_2 (g)

$Mg(NO_3)_2$ (s) $\rightarrow$ MgO (s) + 2 NO_2 (g) + ½ O_2 (g)

NaOH(aq) reacts with the acidic CO_2 and NO_2 gas produced from the thermal decomposition of $MgCO_3$ and $Mg(NO_3)_2$.

The gas collected in the gas syringe is O_2.

(ii) $Mg(NO_3)_2$ (s) $\rightarrow$ MgO (s) + 2 NO_2 (g) + ½ O_2 (g)

Amount of O_2 gas collected = $\frac{78}{24000}$ = 0.00325 mol

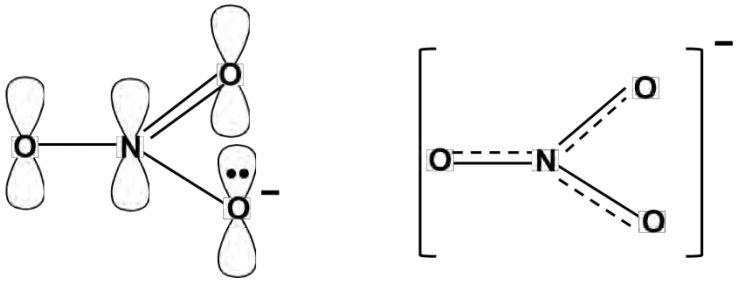
Amount of $Mg(NO_3)_2$ = 2 $\times$ 0.00325 = 0.0065 mol

Mass of $Mg(NO_3)_2$ = 0.0065 $\times$ (24.3+14$\times$2+16$\times$6) = 0.9640 g

% by mass of $Mg(NO_3)_2$ in mixture = $\frac{0.9640}{2.50} \times 100\%$ = 38.6 %

b) In NO_3^-, the presence of continuous overlap of p–orbitals across the 3 oxygen atoms and the nitrogen atom allows the π electrons to be delocalised.

As a result, all the three NO bonds in NO_3^- are intermediate bond between an N–O bond and N=O bond. (NO bond length in NO_3^- is between that of N–O bond and N=O bond)



c) (i) The ionic radius of Mg^{2+}, Ca^{2+} and Ba^{2+} are 0.065 nm, 0.099 nm and 0.135 nm respectively. Down Group II, the ionic charge remains the same while the ionic radius increases, hence charge density decreases down the group.

Mg^{2+} has the greatest polarising power , thus it can distort the electron cloud of CO_3^{2-} to a larger extent. The C–O covalent bond in $MgCO_3$ is weakened more significantly and less amount of energy is required to decompose $MgCO_3$.

As a result, $MgCO_3$ decomposes more readily than $CaCO_3$ and $BaCO_3$ as it produces the largest amount of CO_2 in the same time period.

Solution

(ii) Since the thermal stability of Group II carbonates increases down the group, $SrCO_3$ is more stable than $CaCO_3$ but less stable than $BaCO_3$.

Volume of CO_2 produced in the same time interval is between 5–25 cm^3

d) The solubility of Group II carbonates decreases down the group. Due to the relatively larger size of the anion CO_3^{2-}, the change in lattice energy of Group II carbonate is not significant. However, as charge density decreases down the group, the enthalpy change of hydration of Group II ions becomes less exothermic down the group.

Since $\Delta H_{soln} = \Delta H_{hyd} - L.E.$

ΔH_{soln} for Group II carbonates becomes less exothermic down the group, explaining the decreasing trend of their solubility.

e) (i) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

HCO_3^- acts as a base and releases OH^- upon dissociation in water.

(ii) Working range of phenolphthalein is pH 8–10. When phenolphthalein changes colour, it indicates the first reaction between CO_3^{2-} and H^+ is completed.

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$

Amount of HCl used = $\frac{20.00}{1000} \times 0.05 = 0.001$ mol

Amount of CO_3^{2-} reacted = 0.001 mol

Concentration of Na_2CO_3 in 10.0 cm^3 sample = $0.001 \div \frac{10.0}{1000} = 0.1$ mol dm^{-3}

(iii) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$

$2.13 \times 10^{-4} = \frac{[OH^-]^2}{0.1}$

$[OH^-] = 0.004615$ mol dm^{-3}

pOH = 2.336

pH = 14 – pOH = 11.67

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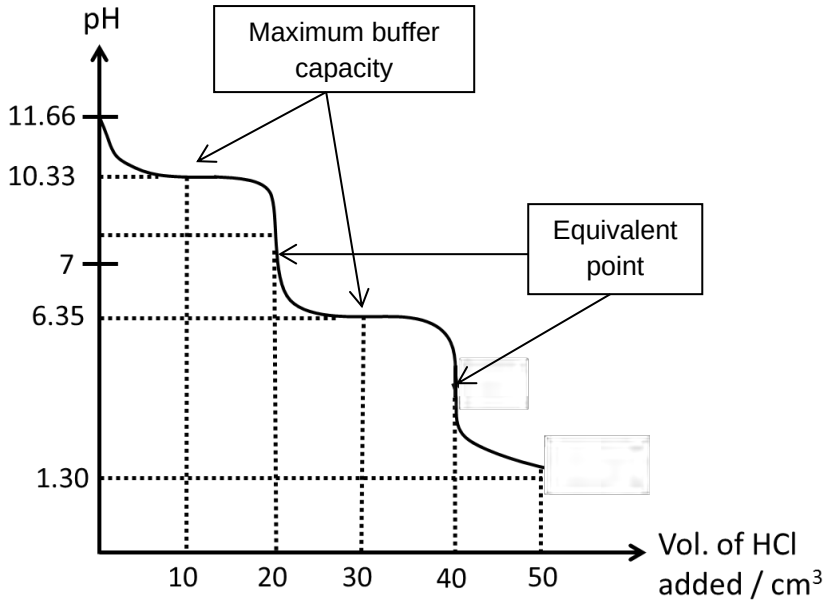
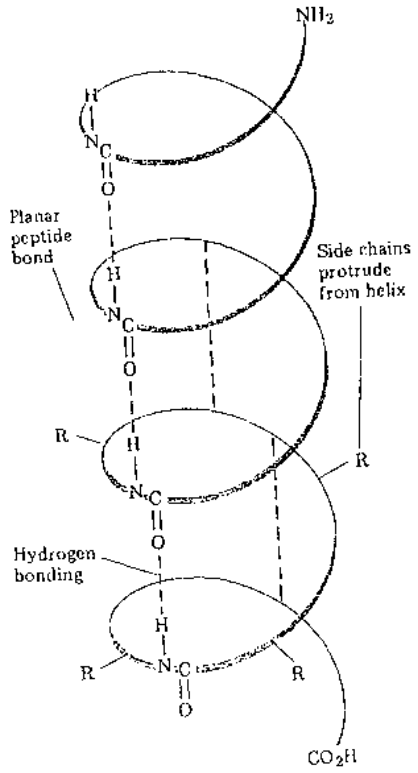
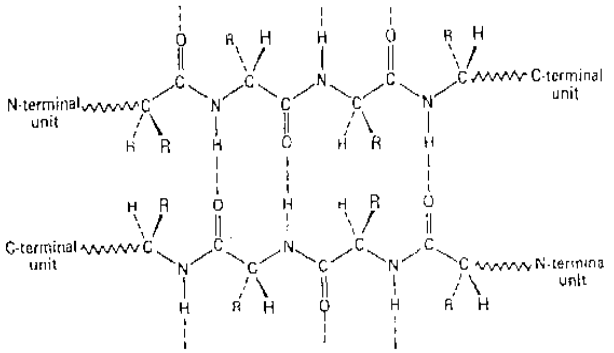
Solution

(iv)



5 a) (i) Primary protein structure refers to the <u>unique sequence of amino acids</u> joined by **peptide bonds** in a polypeptide chain.





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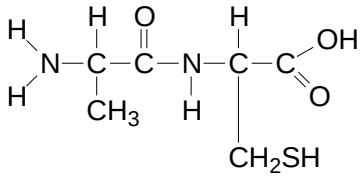
Solution

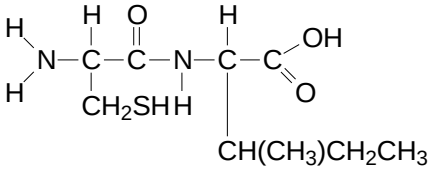
(iii) Globular

There are 8 **α helices** on the outside which are the hydrophilic side chains that will be in contact with water.There are 8 **parallel β-strands** on the inside which are the hydrophobic chains that will cluster inside the folds to be away from water.

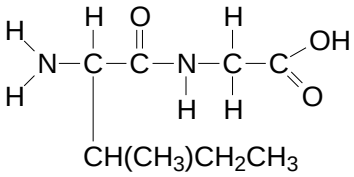
(iv) 4



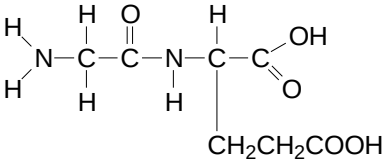
Ala-Cys



Cys-Ile



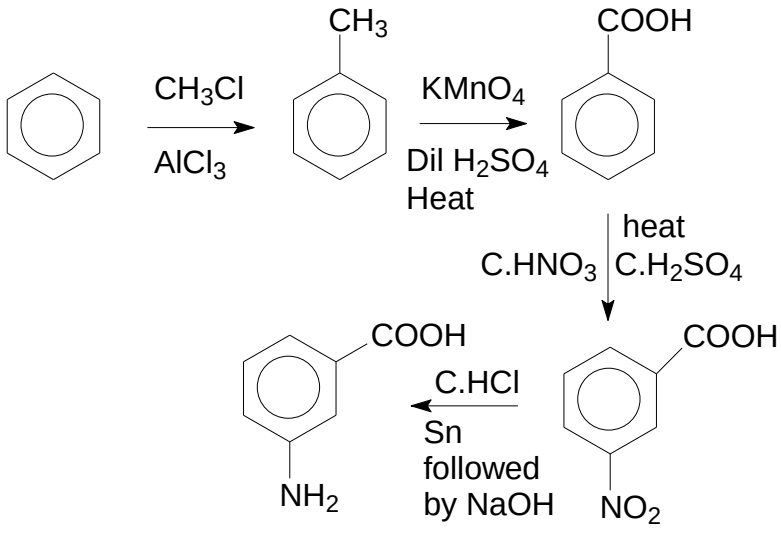
Ile-Gly



Gly-Glu

(v) Ionic interaction and hydrogen bonding

5 b)



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Solution

5 c) (i) 4-methylphenylamine will have a lower pK_b value. The $–CH_3$ group in 4-methylphenylamine is electron donating. It exerts an electron-donating inductive effect, thus increasing the electron density around the nitrogen. Greater availability of the lone pair of electrons to form a dative bond with a proton. Hence, 4-nitrophenylamine is a weaker base than phenylamine

Or

In the methylphenylammonium ion, the electron releasing alkyl group offsets the positive charge on the N, causing it to have a lower tendency to lose a H^+ in order to react with the OH^- to form H_2O.

5 c) (ii) Reagent: CH_3CH_2COCl

Condition: Room temperature

5 c) (iii) Test: NaOH(aq), Heat

Observations: alkaline vapour turning moist red litmus paper blue (**X**)

White precipitate formed (**W**)

c) (iv)