Essay Answers:

1 (a) (i) $PV = nRT$

$m / V = \rho = \dfrac{P \times M_r}{RT}$

$\therefore$ density of $NO_2 = \dfrac{1.01 \times 10^5 \times 46.0}{8.31 \times 298}$

- $= 1880 \text{ g m}^{-3}$ (to 3 s.f)
- $= 1.88 \times 10^{-3} \text{ g cm}^{-3}$

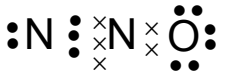
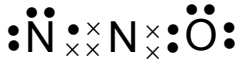
(ii) $NO_2(g) + N_2O(g) \rightarrow 3NO(g)$

- $\Delta H^\theta_r = \sum \Delta H^\theta_f(\text{products}) - \sum \Delta H^\theta_f(\text{reactants})$
  $= 3(+90.4) - (+33.9 + 81.6)$
  $= +155.7 \text{ kJmol}^{-1}$

- At 800 K, $\Delta G_r = \Delta H^\theta_r - T\Delta S^\theta_r$
  $= +155.7 - 800(+171.4 \times 10^{-3})$
  $= +18.6 \text{ kJ mol}^{-1}$

- Since $\Delta G_r > 0$ at 800 K, the reaction is not spontaneous.

(iii)

-  OR 

[Correct number of dots and crosses for N and 2 O atoms.]

- Linear molecule

(b)

- For AgCl to precipitate , $[Ag^+][Cl^-] > 1.8 \times 10^{-10}$
  $(1.8 \times 10^{-2}) \times [Cl^-] > 1.8 \times 10^{-10}$
  $[Cl^-] > 1.8 \times 10^{-8} \text{ mol dm}^{-3}$

- For $PbCl_2$ to precipitate, $[Pb^{2+}][Cl^-]^2 > 1.7 \times 10^{-5}$
  $(2.0 \times 10^{-2}) \times [Cl^-]^2 > 1.7 \times 10^{-5}$
  $[Cl^-] > 2.9 \times 10^{-2} \text{ mol dm}^{-3}$

- AgCl will precipitate out from the solution first as it requires a much smaller concentration of Cl^-.

(c) (i)

- $X^+(g) \rightarrow X^{2+}(g) + e$
- Going down the X^+ ions of Group II, both the nuclear charge and screening effect increase. As the <u>increase in screening effect outweighs the increase in nuclear charge</u>, the effective nuclear charge of the X^+ cations decreases down the group.
- Hence moving down the group, the valence electron in the X^+ cation becomes <u>further away from the nucleus</u> and is <u>less strongly attracted</u>, thus needing less energy for its removal.

(ii)

- Mg^{2+} ion has a <u>higher charge density</u> than Ba^{2+} ion and hence is more polarising. Mg^{2+} ions <u>polarise the large NO_3^- ions to a greater extent</u> and hence causes the N – O bonds to be weakened. Thus $Mg(NO_3)_2$ is less thermally stable and decomposes at a lower temperature than $Ba(NO_3)_2$.
- Equations:
  $Mg(NO_3)_2 \rightarrow MgO + ½\ O_2 + 2NO_2$
  $Ba(NO_3)_2 \rightarrow BaO + ½\ O_2 + 2NO_2$

(iii)

- **M** is magnesium.
- $MgCO_3$ undergoes <u>decomposition</u> when heated. Since it forms $CO_2(g)$ which escapes when it is formed, there is a loss in mass during heating.
  $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
- When **X** which is MgO is added to water, it reacts to form <u>insoluble $Mg(OH)_2$</u>. As the concentration of aqueous OH^- is low, the resulting solution is only weakly alkaline.
  $MgO + H_2O \rightarrow Mg(OH)_2$
- Adding $H_2SO_4(aq)$ to the above mixture produces <u>$MgSO_4$ which is soluble in water</u>. Hence no precipitate is observed.
- 1 mark for the two equations for decomposition of $MgCO_3$ and reaction of MgO with water.

2 (a) $NaOH(s) + aq \rightarrow NaOH(aq)$

$\Delta H_{sol} = \Delta H_{f\ of\ NaOH\ (aq)} - \Delta H_{f\ of\ NaOH\ (s)} = -470 - (-425)$ ● $= -45.0\ kJ\ mol^{-1}$

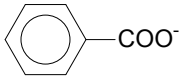
Number of moles of NaOH = $\frac{10.0}{40}$ = 0.250 mol

- Heat evolved = 45 x 0.25 = 11.3 kJ
- Temperature increase = $\frac{Q}{mc} = \frac{11.3 \times 1000}{(250)(4.18)}$ = 10.8 °C

(b) (i) $[H^+] = \sqrt{K_a.c} = \sqrt{10^{-8.35} \times 0.1} = 2.11 \times 10^{-6}\ mol\ dm^{-3}$

- $pH = -lg[H^+] = 4.68$

(ii)

- Benzoic acid is a <u>stronger acid</u> as it has a lower pK_a value.
- For phenoxide ion formed from the dissociation of 3-nitrophenol, the lone pair of electrons on oxygen is delocalised into the benzene ring and the nitro group being electron withdrawing further disperses the negative charge on the phenoxide ion resulting in a stable anion formed. However benzoic acid is a stronger acid as  is <u>more stable</u> than phenoxide ion due to the <u>delocalisation of negative charge over two electronegative oxygen atoms</u>, resulting in a much more stabilised ion as the <u>negative charge is better dispersed and is more likely to release H^+.</u>

(iii)

- Phenolpthalein and bromothymol blue are both weak acids. Small amounts are used so that it will not affect accuracy of the end-point titre value. (If larger amounts are used, a larger titre value will be obtained)

(iv) ● **A**: pH = 4.20 ● **B**: Volume of titre = 7.20 cm^3

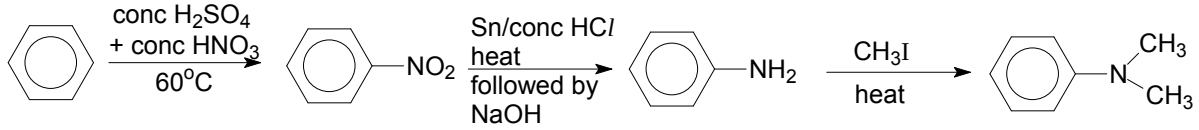
(v) (first endpoint with bromothymol blue)

● concentration of benzoic acid = (14.40/1000 x 1) / (25.0/1000) = 0.576 mol dm^{-3}

(second endpoint with phenolphthalein)

● concentration of 3-nitrophenol = (7.60/1000 x 1) / (25.0/1000) = 0.304 mol dm^{-3}

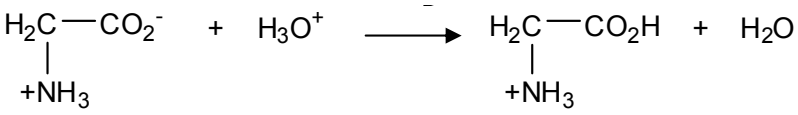
(c) ●●●



(d) **(i)** ● Buffers are solutions that resist changes in pH upon additions of <u>small</u> amounts of acid or alkali.

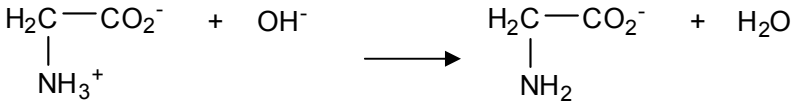
(ii) ● $H_3\overset{+}{N}–CH_2–COO^-$

(iii) ● When small amounts of acid is present,



H^+ is removed thus there is negligible change in pH.

● When small amounts of base is present,



OH^- is removed thus there is negligible change in pH.

(iv) ● $2CH_4 + 2H_2O + NH_3 \rightarrow H_2NCH_2COOH + 5H_2$

(v) ● Large amounts of energy is required to break the strong covalent bonds.

OR Energy is required to overcome activation energy for the reaction

OR Energy is required to break the covalent bonds to form free radicals (also can be accepted)

3. **(a)** • Solution formed is <u>orange (pH~3-4).</u>

• $AlCl_3$ undergoes <u>both hydration and hydrolysis</u> as <u>Al^{3+} has a high charge density</u>, hence a <u>high polarizing power</u>. It draws electrons away from its surrounding water molecules and weakens the O-H bond.

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) \rightarrow [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$

• 1 mark for both equations

(b) **(i)**

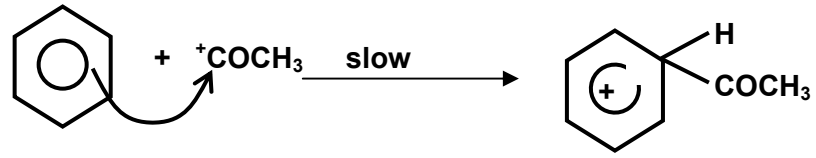
- No, because Al_2Cl_6 is not <u>electron-deficient</u> and is unable to <u>accept a lone pair to form a dative bond</u>.

(ii)

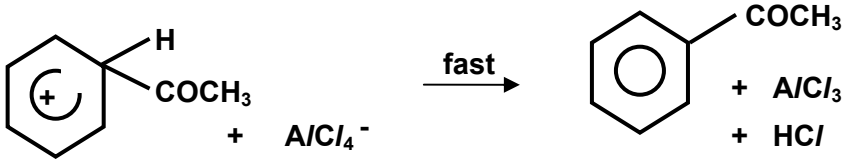
- Step 1: Generation of electrophile

$$AlCl_3 + CH_3COCl \rightleftharpoons {}^{+}COCH_3 + AlCl_4^{-}$$

- Step 2:



- Step 3:



(c) **(i)**

- $SiCl_4$ is a <u>(simple) covalent chloride</u> that <u>undergoes hydrolysis</u> in water. Hydrolysis occurs due <u>to energetically accessible vacant 3d-orbitals</u> available for dative bonding with water.

(ii)

- $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$
- The standard entropy change is positive because <u>4 moles of gas is being produced</u> in the reaction, <u>increasing the degree of randomness / disorderliness</u> of the system.

(iii)

- $SiCl_4 + 4CH_3OH \rightarrow Si(OCH_3)_4 + 4HCl$
- <u>Steamy white fumes</u> will be observed.

(d)

- Since there are <u>5 σ bonds</u> (5 electron pairs) around P, there should be 5 hybrid orbitals. Since there is only 1 3s orbital and 3 3p orbitals, the fifth orbital has to be a 3d orbital. Hence type of hybridization is <u>sp^3d.</u>

(e) **(i)**

- **Y** liberates white fumes with PCl_5, therefore it contains <u>–OH group</u>.
- **Y** forms orange ppt with Brady's reagent, therefore it contains a carbonyl group. **Y** does not react with Tollen's reagent, therefore it can only be a <u>ketone</u>.
- **Y** forms a yellow ppt in the tri-iodomethane test, hence it contains either <u>CH_3CO-R or $CH_3CH(OH)$-R</u> where R is H or an alkyl chain.
- **Y** is oxidised to form a carboxylic acid, hence it must contain a <u>primary alcohol</u>.

Therefore, **Y** must be

- $CH_3COCH_2CH_2OH$

(ii)

- His choice of chemical test was <u>inappropriate</u> because the PCl_5 would have <u>undergone hydrolysis</u> to form phosphoric and hydrochloric acid.
- $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

4. **(a)** **(i)**

- Anode : $Li \rightarrow Li^+ + e^-$
- Cathode : $Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^-$

(ii)

- $\mathbf{E_{Li^+/Li}} = -3.04V$
  $E_{cell} = E_{red} - E_{oxid}$
  $+2.30 = \mathbf{E_{Cu_2O/Cu}} - (-3.04)$
  $\mathbf{E_{Cu_2O/Cu}} = 2.30 - 3.04 = -0.74V$

Assumptions made:

- 298K (25^oC) &
  Concentration of aqueous alkaline electrolyte = 1.0 $moldm^{-3}$

(iii)

- Li, being a Group I metal is reactive and would react with water in the aqueous electrolyte. Hence the Li anode has to be immersed in an organic electrolyte.

(b) (i)

- $Pt(s) \mid CO_2(g) \mid H_2C_2O_4(aq) \parallel Cu_2^+(aq) \mid Cu(s)$

(ii)

1) Effervescence/ Bubbles of CO_2 gas will be seen around the anode (Pt electrode)
2) Reddish-brown Cu electrode will increase in size (grow thicker)
3) Blue colour in the aqueous solution will fade as $[Cu^{2+}]$ decreases.

3 points – 2 marks; 2 points – 1mark; 0 -1 points – 0 mark.

(iii) $Cu^{2+} + 2e^- \rightleftharpoons Cu$

$E^{\ominus}_{Cu^{2+}/Cu} = +0.34$ V (when $[Cu^{2+}] = 1$ mol dm^{-3})

- As the concentration of Cu^{2+} is at 2.0 mol dm^{-3}, by Le Chatelier's Principle, the system will try to decrease the concentration of Cu^{2+} by shifting the position of the above equilibrium to the right. The tendency of Cu^{2+} to be reduced is increased and the actual $E_{Cu^{2+}/Cu}$ is more positive than +0.34 V.
- Since measured $E_{cell} = E_{Cu^{2+}/Cu} - E_{CO_2/H_2C_2O_4}$, the value of E_{cell} would be more positive than +0.83 V.

(c) (i)

- Biuret reagent is a complex ion where aqueous tartrate ions bind to Cu^{2+} ion. Cu^{2+} ion contains partially filled 3d-orbitals where in the presence of ligands, it causes a splitting of the energy of 3d-orbitals into 2 groups with an energy gap between them, ΔE. (crystal field splitting).
- When a d-electron from lower energy group is promoted to the higher energy group (*d-d electron transition*), radiation in the *visible* region of the electromagnetic spectrum corresponding to ΔE is absorbed.
  Hence, the light energy not absorbed will be seen as the colour of the complex. (Complementary colour observed).
- For potassium sodium tartarate, it does not have electrons in the 3d-orbitals and hence these d-d electron transitions would not occur, thus no radiation in the visible region of the electromagnetic spectrum would be absorbed. Hence, these compounds are colourless.

(ii)
- Ligand exchange has occurred.
- Different ligands cause splitting of the d-orbitals resulting in different energy gaps, which correspond to different wavelengths of visible light being absorbed. Hence different colours are observed.

(iii)
- Heavy metal ions such as Cu^{2+} can combine reversibly with the –SH groups in cysteine residues, hence disrupting disulfide bonds.

OR

- Heavy metal ions such as Cu^{2+} can form ionic bonds with the carboxylic acid anions on the side chain of the protein molecule. This will disrupt ionic bonds formed between the side chains of the protein molecule.

(iv)
- By heat
- An increase in temperature causes an increase in kinetic energy and vibration of molecules. This disrupts the whole range of weak interactions (hydrogen bonds, van der Waals attractions, ionic bonds and disulfide linkages) responsible for maintaining the secondary, tertiary and quaternary structure of Keratin.

OR

- By extreme pH changes
- The extreme pH changes can change the charges on the amino acid residues by protonating or deprotonating the R-groups on the side chain of the proteins (e.g. carboxylic acid group in glutamic acid residue or the amino groups of the side chain in lysine residue). This will disrupt the ionic bonds or hydrogen bonds between the side chains of the protein molecule.

(d) (i)
- $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

OR

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 6H_2O$

Because of context of question, equations starting from $Cu(OH)_2$ cannot be accepted.

(ii)
- CN^- - Monodentate
  Coordination number = 4

5 (a) (i)
- The overall 3-dimensional shape of a protein formed by the folding of the secondary structure of the protein to minimize exposure of the hydrophobic groups and expose the hydrophilic groups to water. The folds are held by ionic, disulphide, hydrogen bonding or van der Waals interactions.

(ii)
- Reflux with NaOH(aq) or HC*l* for several hours

(b) (i)
- 6

(ii)
- $M_r = 3 \times 75 + 2 \times 89 + 2 \times 165 - 6 \times 18 = 625$

(c) (i)
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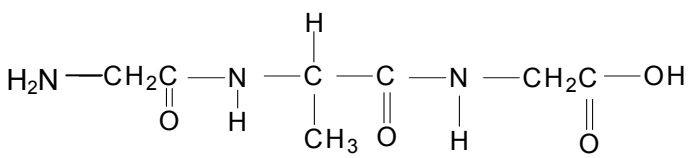
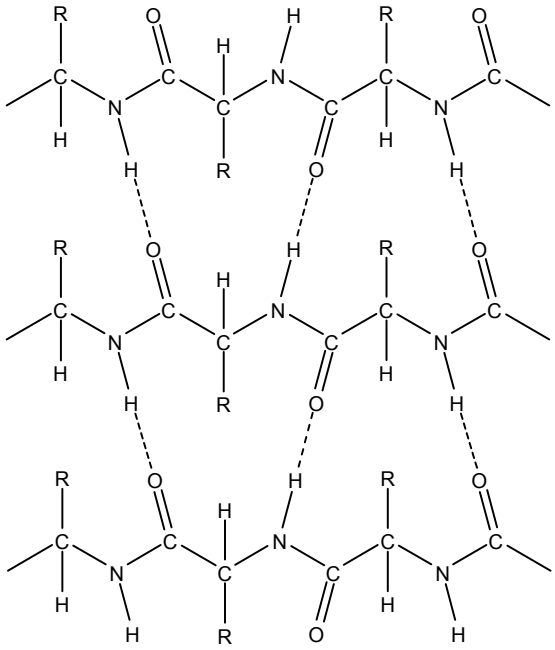


(ii)
- Condensation

(iii)
- The highly electronegative N and O in the structure is involved in hydrogen bonding to form the secondary and tertiary structures and hence not able to form hydrogen bonds with water molecules.
- The exposed R groups are non-polar and hence silk is hydrophobic.

(iv)
- diagram showing alternating R groups, zig zag shape and hydrogen bonding clearly labelled
- Mention hydrogen bonding in description or in diagram



(d) **(i)**
- Irradiation of Cl_2 results in homolytic cleavage to give Cl radicals which are highly reactive. Reaction starts immediately. When irradiation stops, the
- radicals are still being regenerated and the reaction continues.

•• Mole ratio of 1°, 2° and 3° monochlorinated products 6 : 1 : 1

(iii) $\Delta H = -\Delta H_{RCl} - \Delta H_{HCl} + \Delta H_{RH} + \Delta H_{Cl\text{-}Cl}$

- For 1° Hydrogen $\Delta H = -107$ kJ mol^{-1}
- For 2° Hydrogen $\Delta H = -127$ kJ mol^{-1}
- For 3° Hydrogen $\Delta H = -129$ kJ mol^{-1}

(iv)
- From (iii), the enthalpy change becomes more negative for the substitution of 1° to 3° hydrogen implying that the formation of 2-chloro-2,4-dimethylpentane
- is more spontaneous. A factor that could give rise to this result is the strength of C-H bonds/relative stability of the alkyl radicals.

(v)
- The tertiary hydrogen radical formed is more stable than the secondary hydrogen radical.