Chemistry (Theory)

[Time allowed: 3 hours] [*Maximum marks:70]*

General Instructions:

(i) All questions are compulsory.
(ii) Marks for each question are indicated against it.
(iii) Question numbers **1** to **8** are very short-answer questions and carry **1** mark each.
(iv) Question numbers **9** to **18** are short-answer questions and carry **2** marks each.
(v) Question numbers **19** to **27** are also short-answer questions and carry **3** marks each.
(vi) Question numbers **28** to **30** are long-answer questions and carry **5** marks each.
(vii) Use Log Tables, if necessary. Use of calculators is not allowed.

Q28. (a) What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it.

(b) In the button cell, widely used in watches, the following reaction takes place

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$$

Determine E° and ΔG° for the reaction.

$$\left(\text{given: } E^\circ_{Ag^+/Ag} = +\,0.80\text{V},\ E^\circ_{Zn^{2+}/Zn} = -0.76\text{V}\right)$$ **5**

OR

(a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.

(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500Ω. What is the cell constant if the conductivity of 0.001 M KCl solution 298 K is 0.146×10^{-3} S cm^{-1}?

Ans. (a) A lead storage battery has a secondary cell. Thus, it can be recharged by passing direct current through it. Therefore, it can be reused.
It is used in automobiles.
In a lead storage cell, the anode is made of spongy lead and the cathode is a grid of lead packed with lead dioxide. The electrolyte used is H_2SO_4.
At anode:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$$

At cathode:

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

Overall cell reaction:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$$

(b) From the given reaction, it is known that zinc is oxidised and silver is reduced in the button cell.

The reactions occurring at the anode and cathode are –

Anode: $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode: $Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)}$

$$\begin{aligned} \text{Now, } E^0_{cell} &= E^0_{cathode} - E^0_{anode} \\ &= E^0_{Ag^+/Ag} - E^0_{Zn^{2+}/Zn} \\ &= 0.80 - (-0.76) \\ &= 1.56\ V \end{aligned}$$

We know that

$\Delta_r G^0 = -nE^0 F$

Here,

$n = 2$

F = 96500 C mol^{-1}

$$\begin{aligned} \Delta_r G^0 &= -2 \times 1.56 \times 96500\ J\ mol^{-1} \\ &= -301080\ J\ mol^{-1} \end{aligned}$$

OR

(a) Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section *A* and distance of unit length.

$$\Lambda_m = \kappa \frac{A}{l}$$

Now, l = 1 and A = V (volume containing 1 mole of the electrolyte).

$\therefore\ \Lambda_m = \kappa V$

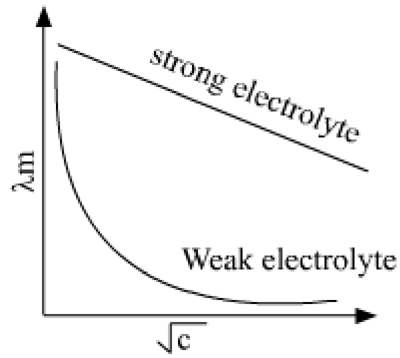
Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution.

Variation of molar conductivities with dilution:

For strong electrolytes, molar conductivity slowly increases with dilution.

For weak electrolytes, molar conductivity increases steeply on dilution, especially near lower concentrations.

The variation of Λ_m with $\sqrt{c}$ for strong and weak electrolytes is shown in the following plot:



(b) Given,
Conductivity, $\kappa = 0.146 \times 10^{-3}$ S cm^{-1}
Resistance, $R = 1500\ \Omega$

$\therefore$ Cell constant $= \kappa \times R$
$= 0.146 \times 10^{-3} \times 1500$
$= 0.219$ cm^{-1}

Q29. (a) Illustrate the following name reaction giving suitable example in each case:
(i) Clemmensen reduction
(ii) Hell-Volhard-Zelinsky reaction

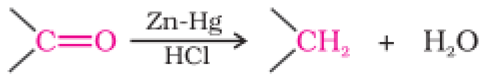
(b) How are the following conversions carried out?
(i) Ethylcyanide to ethanoic acid
(ii) Butan-l-ol to butanoic acid
(iii) Benzoic acid to m-bromobenzoic acid **5**

OR

(a) Illustrate the following reactions giving a suitable example for each.
(i) Cross aldol condensation
(ii) Decarboxylation

(b) Give simple tests to distinguish between the following pairs of compounds
(i) Pentan-2-one and Pentan-3-one
(ii) Benzaldehyde and Acetophenone
(iii) Phenol and Benzoic acid

Ans. (a) (i) <u>**Clemmensen Reduction**</u>
The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-amalgam and concentrated hydrochloric acid. This is known as Clemmensen reduction.



(Clemmensen reduction)

(ii) **<u>Hell-Volhard-Zelinsky (HVZ)reaction.</u>**

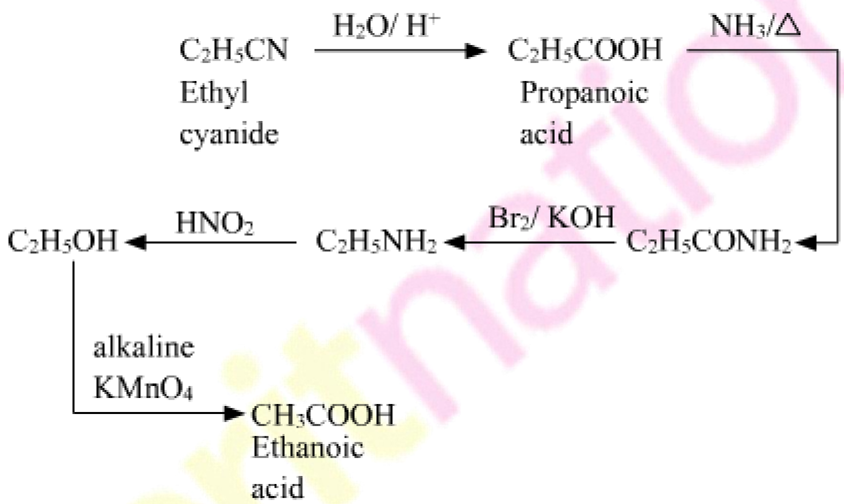
Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.

$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red phosphorus}} R\text{-}\underset{\substack{|\\ X}}{CH}\text{-}COOH$$

X = Cl, Br

α – Halocarboxylic acid

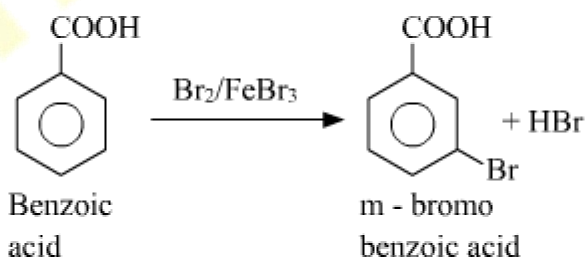
(b) (i)



(ii)

$$\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{(ii) Dil. } H_2SO_4]{\text{(i)} K_2Cr_2O_7/H_2SO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

(iii)



OR

(a) (i) **Cross aldol condensation:**

When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, it gives a mixture of four products.

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta]{1.\ NaOH} \underset{\text{But-2-enal}}{CH_3\text{-}CH{=}CH\text{-}CHO} + CH_3CH_2\text{-}CH{=}\underset{\substack{|\\CH_3}}{C}\text{-}CHO$$

$$+\ \underset{\text{2-Methylbut-2-enal}}{CH_3\text{-}CH{=}\underset{\substack{|\\CH_3}}{C}\text{-}CHO} + \underset{\text{Pent-2-enal}}{CH_3CH_2\text{-}CH{=}CHCHO}$$

(ii) Decarboxylation refers to the reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda-lime.

$$\underset{\text{Sodium ethanoate}}{CH_3 - COONa} \xrightarrow[\Delta]{\text{Soda-lime (mixture of NaOH and CaO in 3:1 ratio)}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(b) (i) Pentan-2-one and pentan-3-one can be distinguished by iodoform test. Pentan-2-one is a methyl ketone. Thus, it responds to this test. But pentan-3-one not being a methyl ketone does not respond to this test.

$$\underset{\text{Pentan} - 2 - \text{one}}{CH_3CH_2CH_2 - \overset{\overset{O}{\|}}{C} - CH_3} + 3\ NaOI \longrightarrow \underset{\text{Sodium butanoate}}{CH_3CH_2CH_2COONa} + \underset{\substack{\text{Iodoform}\\\text{(yellow ppt)}}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Pentan} - 3 - \text{one}}{CH_3CH_2 - \overset{\overset{O}{\|}}{C} - CH_2CH_3} + NaOI \longrightarrow \text{No yellow ppt of iodoform}$$

(ii) Benzaldehyde (C_6H_5CHO) and acetophenone ($C_6H_5COCH_3$) can be distinguished by iodoform test.
Acetophenone, being a methyl ketone on treatment with I_2/NaOH undergoes iodoform reaction to give a yellow ppt. of iodoform. On the other hand, benzaldehyde does not give this test.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI$$
$$\downarrow$$
$$C_6H_5COONa + \underset{\text{Iodoform}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{NaOI} \text{No yellow ppt of iodoform}$$

(iii) Phenol and benzoic acid can be distinguished by ferric chloride test.

Ferric chloride test:
Phenol reacts with neutral $FeCl_3$ to form ferric phenoxide complex giving violet colouration.

$$\underset{\text{Phenol}}{6\ C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Iron-phenol complex}\\ \text{(Violet colour)}}}{\left[Fe\ (OC_6H_5)_6\right]^{3-}} + 3H^+ + 3Cl^-$$

But benzoic acid reacts with neutral $FeCl_3$ to give a buff coloured precipitate of ferric benzoate.

$$\underset{\text{Benzoic acid}}{3\ C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate}\\ \text{(Buff coloured ppt)}}}{(C_6H_5COO)_3Fe} + 3\ HCl$$

Q30. (a) Draw the molecular structures of following compounds: **5**

(i) XeF_6
(ii) $H_2S_2O_8$

(b) Explain the following observations:

(i) The molecules NH_3 and NF_3 have dipole moments which are of opposite direction.
(ii) All the bonds in PCl_5 molecule are not equivalent.
(iii) Sulphur in vapour state exhibits paramagnetism.

OR

(a) Complete the following chemical equations:

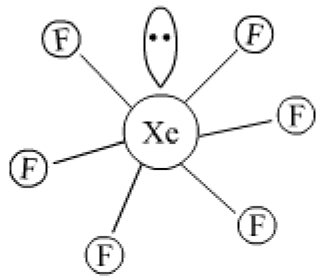
(i) $XeF_4 + SbF_5 \rightarrow$
(ii) $Cl_2 + F_2\ \text{(excess)} \rightarrow$

(b) Explain each of the following:

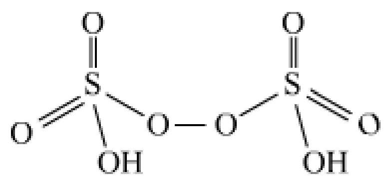
(i) Nitrogen is much less reactive than phosphorus.
(ii) The stability of +5 oxidation state decreases down group 15.
(iii) The bond angles (O – N – O) are not of the same value in NO_2^- and NO_2^+.

Ans.

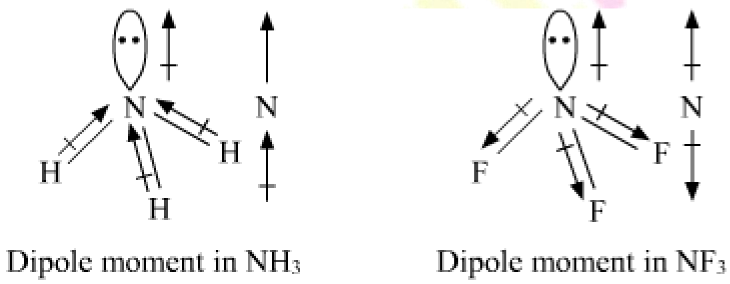
(i) XeF_6
Distorted octahedral



(ii) $H_2S_2O_8$



(b) (i) This is due to the fact that in NH_3, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N – H bonds. On the other hand, in NF_3, the orbital dipole due to lone pairs is in opposite direction as the resultant dipole moment. The diagram given below illustrates this.



(ii) In gaseous and liquid state, PCl_5 has a trigonal bipyramidal structure. In this structure, the two axial P – Cl bonds are longer and less stable than the three equatorial P – Cl bonds. This is because of the greater bond pair – bond pair repulsion in the axial bonds. Hence, all the bonds in PCl_5 are not equivalent.

(iii) In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2. Hence it exhibits paramagnetism.

OR

(a)

(i) $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$
(ii) $Cl_2 + 3F_2$ (excess) $\rightarrow 2ClF_3$

(b) (i) Nitrogen is chemically less reactive. This is because of the high stability of its molecule, N_2. In N_2, the two nitrogen atoms form a triple bond. This triple bond has very high bond strength, which is very difficult to break. It is because of nitrogen's small size that it is able to form pπ–pπ bonds with itself. This property is not exhibited by atoms such as phosphorus. Thus, nitrogen is less reactive than phosphorus.

(ii) On moving down the elements of group 15, the stability of +5 oxidation state decreases. This is due to the reluctances of *s*-electrons to participate in the bond formation. This is known as **inert pair effect.** It is the result of ineffective shielding of *s*-electrons of the valence shell by intervening *d*-and *f*-electrons.

(iii) The difference in bond angle is due to the fact that NO_2^+ has linear shape but NO_2^- has bent shape.