

LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours

ASSIGNMENT PAPER 5

Part A

1. (D) 2. (D) 3. (C) 4. (B) 5. (B) 6. (C) 7. (B) 8. (B) 9. (B) 10. (B) 11. (C) 12. (B) 13. (A) 14. (D)
15. (A) 16. (B) 17. (B) 18. (B) 19. (A) 20. (C) 21. (B) 22. (A) 23. (D) 24. (A) 25. (B) 26. (A)
27. (B) 28. (D) 29. (A) 30. (C) 31. (D) 32. (B) 33. (D) 34. (B) 35. (D) 36. (B) 37. (C) 38. (C)
39. (A) 40. (B) 41. (A) 42. (D) 43. (D) 44. (B) 45. (A) 46. (D) 47. (C) 48. (D) 49. (A) 50. (B)



Part B

Section A

➤ Write the answer of the following questions : (Each carries 2 Mark)

1.

➤ "The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance"

➤ When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases.

➤ The conductivity of electrolytic (ionic) solution depends on :

- (i) The nature of the electrolyte added
- (ii) The size of the ions produced and their solvation
- (iii) The nature of the solvent and its viscosity
- (iv) Concentration of the electrolyte
- (v) Temperature (it increases with the increase of temperature)

2.

➤ $I = 5 \text{ A}$

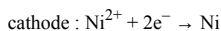
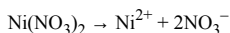
$$t = 20 \text{ min}$$

$$= 20 \times 60$$

$$= 1200 \text{ sec}$$

$$F = \frac{I \times t}{96,500} = \frac{5 \times 1200}{96,500}$$

$$\therefore F = 0.06217 \text{ F}$$



2 mol electron gives 1 mol Ni

$$\therefore 2F \text{ give } \rightarrow 58.7 \text{ g Ni}$$

$$\therefore 0.06217 \text{ give } \rightarrow (?)$$

$$= \frac{0.06217 \times 58.7}{2} = 1.82 \text{ g}$$

3.

➤ "First order reaction means that the rate of reaction is proportional to the first power of the concentration of the reactant R."

➤ For example, consider the following reaction



➤ Rate of reaction for this reaction can be expressed as

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]$$

$$\text{Or } \frac{d[\text{R}]}{[\text{R}]} = -k \text{ dt}$$

➤ Integrating this equation, we get

$$\ln [\text{R}] = -kt + I \dots \text{Eq. (1)}$$

where, I is the constant of integration and its value can be determined easily.

➤ When $t = 0$, $R = [\text{R}]_0$, where $[\text{R}]_0$ is the initial concentration of the reactant.

➤ Therefore, equation (1) can be written as

$$\ln [\text{R}]_0 = -k \times 0 + I$$

$$\ln [\text{R}]_0 = I$$

➔ Substituting the value of I in equation (1)

$$\ln [R] = -kt + \ln [R]_0 \dots \text{Eq. (2)}$$

➔ Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

$$\text{or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \dots \text{Eq. (3)}$$

➔ At time t_1 from equation (1)

$$\ln [R]_1 = -kt_1 + \ln [R]_0 \dots \text{Eq. (4)}$$

At time t_2

$$\ln [R]_2 = -kt_2 + \ln [R]_0 \dots \text{Eq. (5)}$$

where, $[R]_1$ and $[R]_2$ are the concentration of the reactants at time t_1 and t_2 respectively.

➔ Subtracting Eq. (5) from (4)

$$\ln [R]_1 - \ln [R]_2 = -kt_1 - (-kt_2)$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \dots \text{Eq. (6)}$$

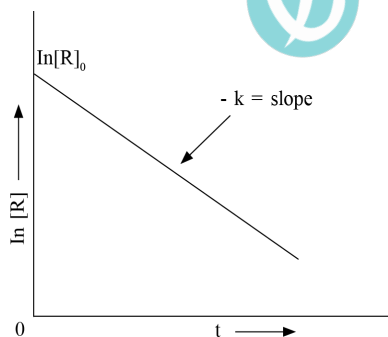
➔ So, equation (2) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both the side

$$[R] = [R]_0 e^{-kt} \dots \text{Eq. (7)}$$

➔ Comparing equation (2) with $y = mx + c$, if we plot $\ln [R]$ against t , we get a straight line with slope = $-k$ and intercept equal to $\ln [R]_0$



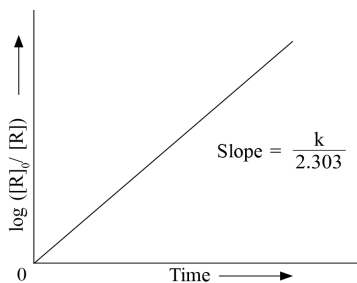
➔ The first order rate equation (3) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \dots \text{Eq. (8)}$$

$$\text{or } \log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

➔ If we plot a graph between $\log \frac{[R]_0}{[R]}$ vs t ,

$$\text{the slope} = \frac{k}{2.303}$$

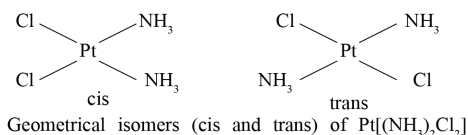


4.

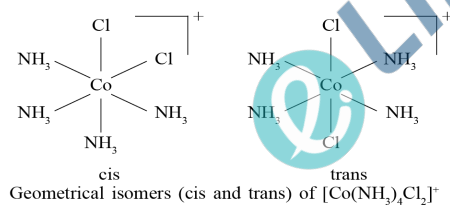
- (1) $K_2 [Zn (OH)_4]$ – potassium tetrahydrozincate(II)
- (2) $K_3 [Cr (C_2O_4)_3]$ – potassium trioxalatochromate (III)

5.

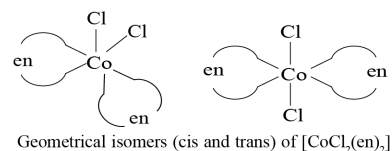
- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.
- Important examples of these behaviour are found with coordination numbers 4 and 6.
- In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer.



- Other square planar complex of the type $MABXL$ (where A, B, X, L are unidentates) shows three isomers-two cis and one trans.
- Such isomerism is not possible for a tetrahedral geometry.
- In octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented cis or trans to each other



- This type of isomerism also arises when didentate ligands L-L [e.g., en] are present in complexes of formula $[MX_2(L-L)_2]$

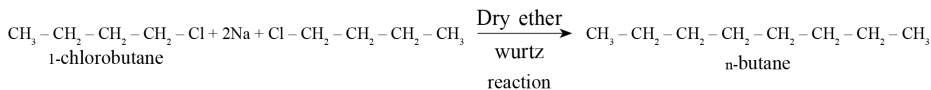


- Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[Co(NH_3)_3(NO_2)_3]$.
- If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, it forms the facial (fac) isomer.
- When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.



6.

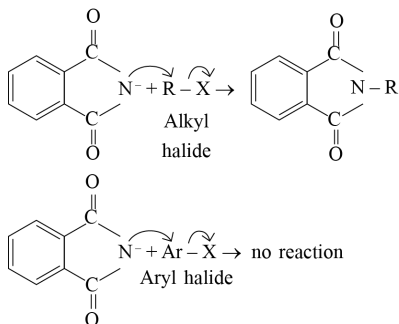
➔ 1-Chlorobutane to n-octane :



7.

➔ The success of the gabriel phthalimide synthesis rests on the nucleophilic attack of phthalimide ion on the organic halide compound.

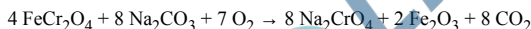
➔ Aryl halides can not be converted to aryl amines by Gabriel synthesis because they do not undergo nucleophilic substitution with potassium phthalimide. So, aromatic primary amines can not be prepared by this method.



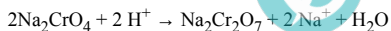
8.

➔ Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore (FeCr_2O_4) with sodium or potassium carbonate in free access of air.

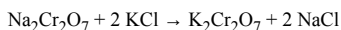
➔ The reaction with sodium carbonate occurs as follows



➔ The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be crystallised.

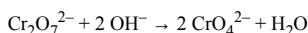
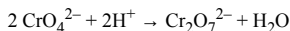


➔ Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.



➔ Orange crystals of potassium dichromate crystallise out.

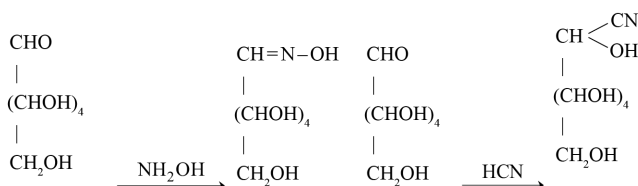
➔ The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.



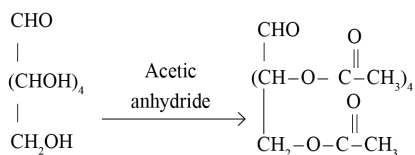
9.

➔ Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin.

These reactions confirm the presence of carbonyl group ($\text{C}=\text{O}$) in glucose.

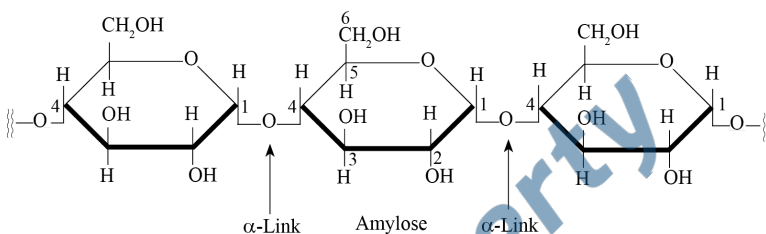


- Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five -OH groups. Since, it exists as a stable compound, five -OH groups should be attached to different carbon atoms.

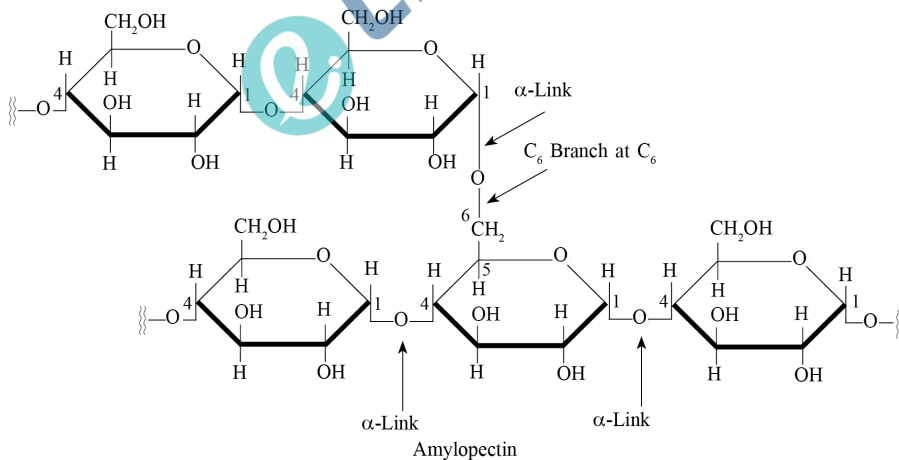


10.

- Starch is the main storage polysaccharide of plants.
- It is the most important dietary source for human beings.
- High content of starch is found in cereals, roots, tubers and some vegetables.
- It is a polymer of α -glucose and consists of two components amylose and amylopectin.
- Amylose is water soluble component which constitutes about 15–20% of starch.
- Chemically amylose is along unbranched chain with 200–1000 α -D-(+)-glucose units held together by C_1 - C_4 glycosidic linkage.



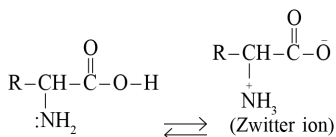
- Amylopectin is insoluble in water and constitutes about 80–85% of starch.
- It is a branched chain polymer of α -D-glucose units in which chain is formed by C_1 - C_4 glycosidic linkage where as branching occurs by C_1 - C_6 glycosidic linkage.



11.

- Amino acids are usually colourless, crystalline solids.
- These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids.
- This behaviour is due to the presence of both acidic (Carboxylic acid group) and basic (amino group) groups in the same molecule.
- "In aqueous solution the carboxyl group can lose a proton and amino group can accept a proton; giving rise to a dipolar ion known as zwitter ion."

➤ This is neutral but contains both positive and negative charges.



➤ In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

12.

➤ Electronic configuration of Mn^{2+} is $[\text{Ar}]183d^5$.

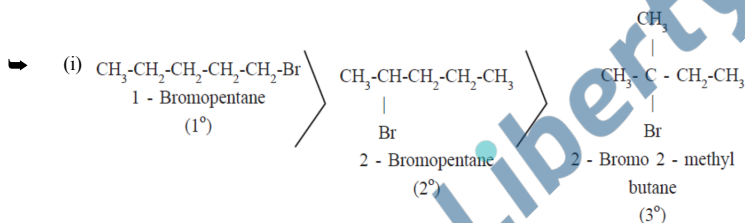
➤ Electronic configuration of Fe^{2+} is $[\text{Ar}]183d^6$.

➤ It is known that half-filled and fully-filled orbitals are more stable. Therefore, Mn in (+2) state has a stable d^5 configuration. This is the reason Mn^{2+} shows resistance to oxidation to Mn^{3+} . Also, Fe^{2+} has $3d^6$ configuration and by losing one electron, its configuration changes to a more stable $3d^5$ configuration. Therefore, Fe^{2+} easily gets oxidized to Fe^{+3} oxidation state.

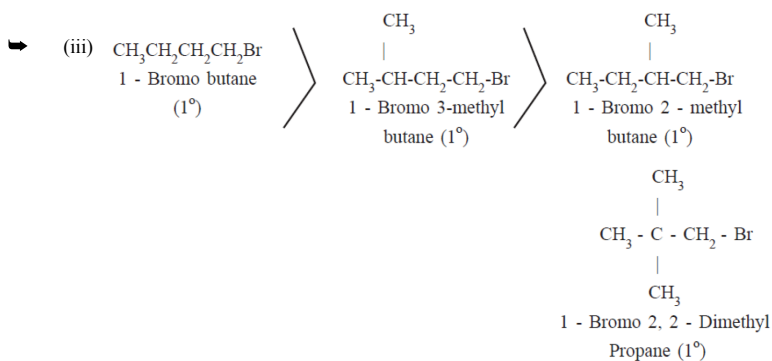
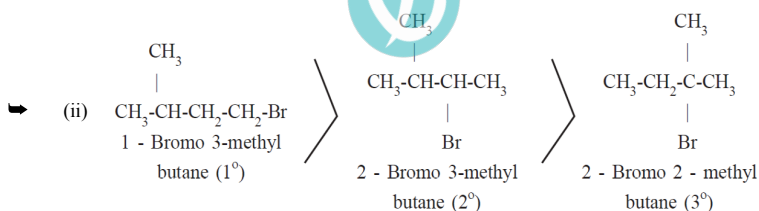
Section B

➤ Write the answer of the following questions : (Each carries 3 Mark)

13.



➤ $\text{S}_{\text{N}}2$ reactivity order : $1^\circ > 2^\circ > 3^\circ$.



➔ The steric hindrance to the nucleophile in the SN^2 mechanism increases with The decrease in the distance of the substituents from the atom containing the leaving group. Further, the steric hindrance increases with an increase in the number of substituents.

➔ Hence, the increasing order of reactivity of the given compounds towards SN^2 displacement is:

➔ 1-Bromo-2, 2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3- methylbutane < 1- Bromobutane

14.

➔ "Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants."

➔ Consider the reaction.



➔ Rate of reaction for this reaction can be expressed as

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]^0$$

➔ As any quantity raised to power zero is units.

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k \times 1$$

➔ Thus, the rate of zero order reaction is independent from concentration of reactants.

$$d[\text{R}] = -k dt$$

➔ Integrating both sides

$$[\text{R}] = -kt + I \dots \dots \text{Eq. (1)}$$

Where, I is the constant of integration

➔ At $t = 0$, the concentration of the reactant $\text{R} = [\text{R}]_0$, where $[\text{R}]_0$ is initial concentration of the reactant.

➔ Substituting in equation (1)

$$[\text{R}]_0 = -k \times 0 + I$$

$$[\text{R}]_0 = I$$

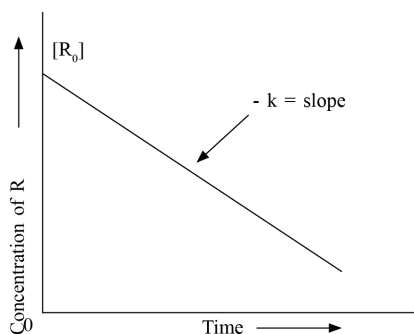
➔ Substituting the value of I in the equation (1)

$$[\text{R}] = -kt + [\text{R}]_0 \dots \dots \text{Eq. (2)}$$

➔ Further simplifying equation (2)

$$k = \frac{[\text{R}]_0 - [\text{R}]}{t} \dots \dots \text{Eq. (3)}$$

➔ Comparing equation (2) with equation of straight line, $y = mx + c$, if we plot $[\text{R}]$ against t , we get a straight line with slope = $-k$ and intercept equal to $[\text{R}]_0$



➔ Half-life for zero order reaction :

➔ For a zero order reaction, rate constant is given by following equation

$$\rightarrow k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{\frac{1}{2}}, [R] = \frac{1}{2} [R]_0$$

The rate constant at $t_{\frac{1}{2}}$ becomes

$$k = \frac{[R]_0 - \frac{1}{2}[R]_0}{t_{\frac{1}{2}}}$$

$$t_{\frac{1}{2}} = \frac{[R]_0}{2k}$$

It is clear that $t_{\frac{1}{2}}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

➔ Half-life for first order reaction :

➔ For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\text{at } t = t_{\frac{1}{2}} [R] = \frac{[R]_0}{2}$$

➔ So, the above equation becomes

$$k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{[R]_0}{\frac{[R]_0}{2}}$$

$$\text{or } t_{\frac{1}{2}} = \frac{2.303}{k} \log 2$$

$$t_{\frac{1}{2}} = \frac{2.303}{k} \times 0.301$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

➔ It can be seen that for a first order reaction, half-life period is constant, i.e. it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{\frac{1}{2}} \propto [R]_0$ for first order reaction $t_{\frac{1}{2}}$ is independent of $[R]_0$

15.

➔ *“Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds.”*

➔ They are usually non stoichiometric and are neither typically ionic nor covalent,

➔ For example, TiC, Mn₄N, Fe₃H, VH_{0.56} and TiH_{1.7}, etc.

➔ These compounds are referred to as interstitial compounds.

➔ The principal physical and chemical characteristics of these compounds are as follows :

▮▮▮ They have high melting points, higher than those of pure metals.

▮▮▮ They are very hard, some borides approach diamond in hardness.

▮▮▮ They retain metallic conductivity.

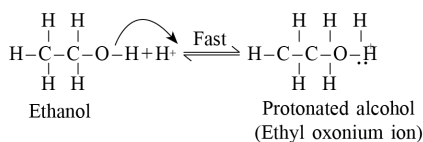
▮▮▮ They are chemically inert.

16.

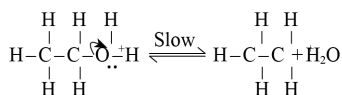
➔ The mechanism of dehydration of ethanol involves the following steps :

➔ Mechanism :

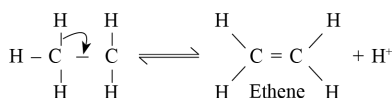
➔ Step 1 : Formation of protonated alcohol



➔ Step 2 : Formation of carbocation : It is the slowest step and hence, the rate determining step of the reaction.



➔ Step 3 : Formation of ethene by elimination of a proton.

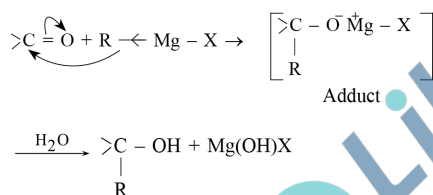


➔ The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

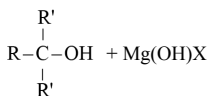
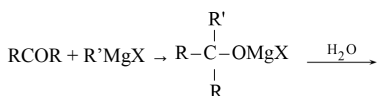
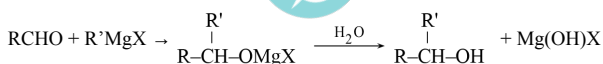
17.

➔ Alcohols are produced by the reaction of Grignard reagents with aldehydes and ketones.

➔ The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



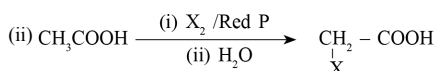
➔ The overall reactions using different aldehydes and ketones are as follows :



➔ You will notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

18.

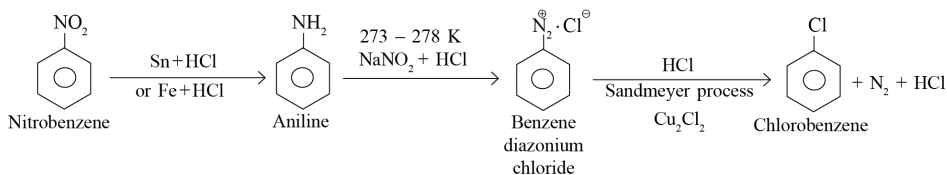
➔ (i) $\text{C}_6\text{H}_5\text{COCl} + \text{SO}_2 + \text{HCl}$



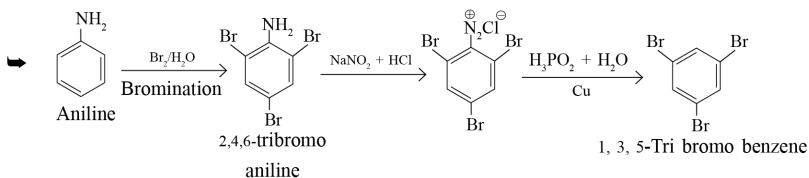
(iii) $\text{CH}_3\text{CH}_2\text{CONH}_2$

19.

➔ Nitrobenzene into chlorobenzene

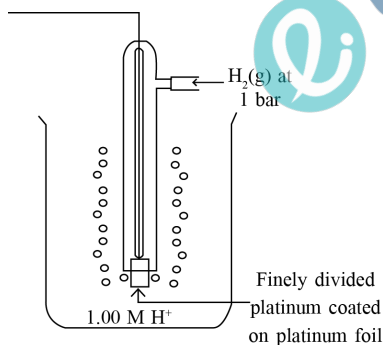


20.

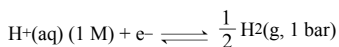


21.

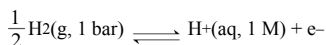
- ➔ Standard Hydrogen Electrode works as a reference electrode for other half cells.
- ➔ The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas bubbled through it.
- ➔ The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity.
- ➔ This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.
- ➔ When this half cell connected to other half cells, To form a complete cell, The SHE can act as cathode or anode.



➔ If it acts as cathode the following reduction reaction takes place on the platinum strip



➔ If it acts as anode the oxidation reaction takes place on the anode



➔ Electrode potential of Standard Hydrogen gas Electrode is accepted zero at all temperature.

Section C

➤ Write the answer of the following questions : (Each carries 4 Mark)

22.

➡ Volume of acetic acid (V) = 0.6 mL,

$$W = 1000 \text{ g}$$

$$\text{density} = 1.06 \text{ g.mL}^{-1}$$

$$\text{Molar mass of acetic acid} = 60 \text{ g.Mol}^{-1}$$

$$\Delta T_f = 0.0205^\circ\text{C}, i = (?)$$

$$K_f = 1.86 \text{ K.kg.Mol}^{-1} \text{ Ka} = (?)$$

$$\text{mass of acetic acid}(W_2) = d \times V$$

$$= 1.06 \times 0.6$$

$$= 0.636 \text{ g}$$

$$\Delta T_f = i \cdot K_f \cdot \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$i = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times W_2 \times 1000} = \frac{0.0205 \times 60 \times 1000}{1.86 \times 0.636 \times 1000}$$

$$i = 1.04$$

$$\alpha = \frac{i - 1}{n - 1}$$

$$= \frac{1.04 - 1}{2 - 1}$$

$$\alpha = 0.04$$

Where, C = Concentration

$$C = \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{0.636 \times 1000}{60 \times 1000}$$

$$= 0.0106 \text{ Mol/L}$$

$$\text{Ka} = \frac{\alpha^2 \cdot C}{1 - \alpha}$$

$$= \frac{(0.04)^2 \cdot (0.0106)}{1 - 0.04}$$

$$= \frac{0.00001696}{0.96}$$

$$\text{Ka} = 1.76 \times 10^{-5}$$

23.

- ➡ Both conductivity and molar conductivity change with the concentration of the electrolyte.
- ➡ Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.
- ➡ The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.
- ➡ This is clear from the equation :

$$G = \frac{\kappa A}{l} = k \text{ (both } A \text{ and } l \text{ are unity in their appropriate units in m or cm)}$$

- ➔ Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length. Therefore,

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

Since $l = 1$ and $A = V$ (volume containing 1 mole electrolyte)

$$\Lambda_m = \kappa V$$

- ➔ Molar conductivity increases with decrease in concentration, this is because the total volume, V, of solution containing one mole of electrolyte also increases.

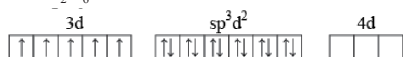
24.

- ➔ Both $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$ and $[\text{Fe}(\text{CN})_6]^{-3}$ complex ions have oxidation state of Fe +3

The electronic configuration of Fe³⁺ is : [Ar] 3d⁵ 4s⁰.

In $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$ complex ion, since H₂O is a weak ligand, the electrons in the 3d orbital are unpaired, hence sp³d² hybridization occurs.

$[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$: [Ar]



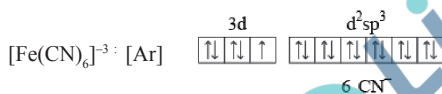
6 H₂O

Provides 6

electron pairs.

- ➔ Thus, $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$ is strongly paramagnetic due to the presence of five unpaired electrons.

In $[\text{Fe}(\text{CN})_6]^{-3}$ complex ion, as CN⁻ is the dominant ligand, the electrons in the 3d orbital are paired, thus forming d²sp³ hybridization.



6 CN⁻

Provides 6

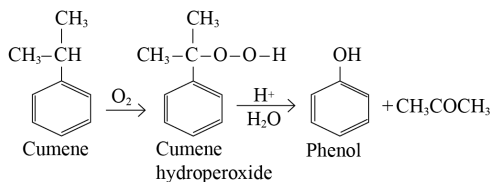
electron pairs.

Thus, $[\text{Fe}(\text{CN})_6]^{-3}$ is weakly paramagnetic due to the presence of one unpaired electron.

25.

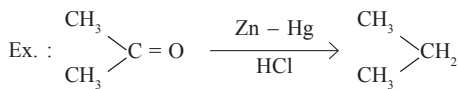
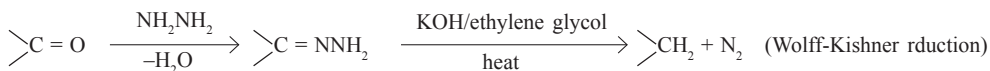
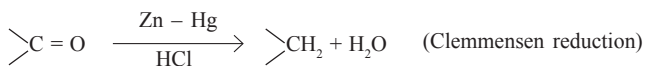
- ➔ From cumene :

- ➔➔➔ Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.



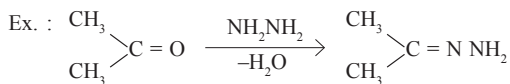
26.

- ➔ Reduction to hydrocarbons: The carbonyl group of aldehydes and ketones is reduced to CH₂ group when treated with zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (Wolff-Kishner reduction).

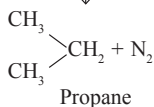
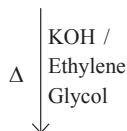


Propanone

Propane



Propanone



27.

➤ Calculation of E_a :

➤ According to Arrhenius equation,

$$k = A e^{-\frac{E_a}{RT}}$$

$$\log k = \log A - \frac{E_a}{2.303RT} \dots \dots (I)$$

➤ Now, $\log k = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T} \dots \dots (II)$

➤ Comparing Eq. (I) and Eq. (II) we get,

$$\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$E_a = 1.25 \times 10^4 \text{ K} \times 2.303 \times R$$

$$E_a = 1.25 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_a = 23.93 \times 10^4 \text{ J mol}^{-1} = 239.3 \text{ kJ mol}^{-1}$$

Calculation of temperature :

➤ For first order reaction

$$k = \frac{0.693}{t_1}$$

$$k = \frac{0.693}{256} = \frac{0.693}{256 \times 60 \text{ s}} = 4.51 \times 10^{-5} \text{ s}^{-1}$$

for given equation,

$$\log k = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\log 4.51 \times 10^{-5} = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$-4.35 = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\frac{1.25 \times 10^4 \text{ K}}{T} = 14.34 + 4.35 = 18.69$$

$$T = \frac{1.25 \times 10^4 \text{ K}}{18.69} = 669 \text{ K}$$