CLASS : XII

SUBJECT – CHEMISTRY

SOLUTIONS

1. (d) They have the same chemical reactivity.
2. (b) Salicylic acid
3. (b) I > II > III
4. (a) Starch
5. (d) Vitamin C
6. (c) Zero order reaction
7. (a) shows large negative deviation from Raoult's law.
8. (a) Osmotic pressure
9. (b) NH_4^+
10. (c) a dehydrohalogenation reaction
11. (b) 0
12. (b) Polypeptides
13. (c) increases with increase in temperature.
14. (a) 0.01 M
15. (d) Assertion (A) is false, but Reason (R) is true.
16. (c) (A) is true, but (R) is false.
17. $P_{solution} = P_A + P_B$

    $= P_A^0X_A + P_B^0X_B$

    $= 160(0.5) + 120\ (0.5)$

    $= 80 + 60$

    $= 140$ mm Hg
18. (i) Mercury cell has a stable electrode potential due to the constant composition of the Electrolyte and electrodes.

(ii) DC is not used because it causes electrolysis, leading to changes in the composition of The solution and polarisation of electrodes, which affects the accuracy of conductance Measurements.

OR

A fuel cell is a device that converts chemical energy into electrical energy through Electrochemical reactions of hydrogen and oxygen, for example, a hydrogen fuel cell. Advantages include higher efficiency, continuous operation as long as fuel is supplied, and Environmentally friendly emissions.

19. (a) For second order kinetics,

    rate R = $K[A]^2$. If [A] is tripled, rate becomes

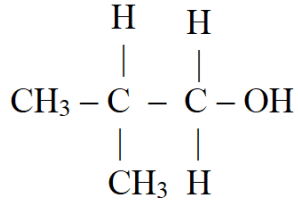
    $R = K(3[A])^2$

    Hence, the rate increases by 9 times.

    (b)) A pseudo first order reaction is a reaction that is inherently of higher order but appears.

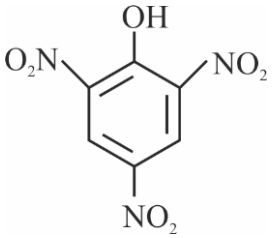
    to be first order due to one reactant being in large excess. Example: Hydrolysis of ester in the presence of excess water.

20. (a)



2-methylpropane-1-ol

(b)



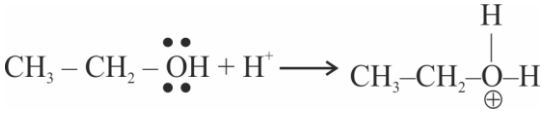
2,4,6-trinitrophenol (picric acid)

21. (a)The electron-withdrawing effect of the hydroxyl group (-OH) in carboxylic acids, decreases the electrophilicity of the carbonyl carbon.

    (b) The carbonyl carbon in propanal (an aldehyde) is more electrophilic than in propanone (a ketone) due to the lack of electron-donating alkyl groups in the aldehyde group.

22. (a) I. $H_2SO_4\ (Conc.) \xrightarrow{Water} H^+ + HSO_4^-$

II.



III. $CH_3-CH_2-\overset{\oplus}{\underset{H}{O}}-H \longrightarrow CH_3-\overset{\oplus}{C}H_2 + H_2O$ (Unstable)

IV. $CH_3-\overset{\oplus}{C}H_2 \longrightarrow CH_2=CH_2 + H^+$

V. $H^+ + HSO_4^- \rightarrow H_2SO_4$

(b) Cumene $+ O_2 \longrightarrow$ (Unstable)

23. ΔT_f (Calculated) = k_f.m

$= k_f \times \frac{W_b}{M_b} \times \frac{1000}{W_a}$

$= 5.12 \times \frac{0.3}{60} \times \frac{1000}{30} = 0.85k$

$i = \frac{\Delta T_f(obs.)}{\Delta T_f(calc.)} \Rightarrow i = \frac{0.45}{0.85}$

i = 0.53

For dimerisation of acetic acid

$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

$i = 1 - \frac{\alpha}{2} \Rightarrow \alpha = 2(1 - i)$

$= 2(1 - 0.53) = 2 \times 0.47$

= 0.94

Percentage of association

$= 0.94 \times 100 = 94\%$

24. (i) Anisole $+CH_3Cl \xrightarrow[\Delta]{\text{Anhydrous } AlCl_3}$

2-methylanisole + 4-methylanisole + HCl

(ii) Phenol $+2[O] \xrightarrow{Na_2Cr_2O_7 + H^+}$ Quinone $+ H_2O$

25. (i) Aniline to p-bromoaniline

Aniline $\xrightarrow[\text{Pyridine}]{(CH_3CO)_2O}$ $\xrightarrow[Br_2]{CH_3COOH}$

$\xrightarrow[H^+]{H_2O}$ p-bromoaniline $+CH_3COOH$

(ii) $\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} CH_3COCl$

$\xrightarrow{NH_3(\text{Excess})} CH_3CONH_2$

$\xrightarrow[\text{Hofmann bromoamide reaction}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$

(iii) Butanenitrile to 1-aminobutane

$CH_3CH_2CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2NH_2$

26. (a) n-Propanol

(b) 2-Bromo-2-methylbutane < 2 – bromopetane < 1 - bromopentane

(c) P-Dichlorobenzene has a symmetrical structure which allows it to pack more efficiently In a crystal lattice, resulting in a higher melting point.

27. The half line time period for the first order reaction is ($t_{1/2}$) =

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

For 1st case : $k_1 = \frac{0.693}{30}$

For 2nd case : $k_2 = \frac{0.693}{10}$

By Arrhenius equation :

$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$\log\frac{0.693}{10}\times\frac{30}{0.693}=\frac{E_a}{2.303\times8.314}\left[\frac{1}{300}-\frac{1}{320}\right]$$

$$\log 3=\frac{E_a}{19.147}\left[\frac{320-300}{96000}\right]$$

$$\frac{0.4771\times19.147\times96000}{20}=E_a$$

E_a = 43848.16 Joule

E_a = 43.84816 kJ

28. $\Delta T_f = i\cdot K_f\cdot m$

Where,

$1 = i\times1.86\times0.5$

$$i=\frac{1}{0.93}\approx1.075\Rightarrow\alpha$$

$$=\frac{i-1}{1}\approx0.075$$

29. (i) Phenylmagnesium bromide (Grignard reagent) is formed.

(ii) $(CH_3)_3\,C–Cl$

(iii) (a) $C_4H_9Cl+NaI\rightarrow C_4H_9I+NaCl$

(b) $CH_3-CH_2-\underset{\text{But-1-ene}}{\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}}-H+HBr \xrightarrow{\text{Peroxide}}$

$$CH_3-CH_2-CH_2-CH_2Br\xrightarrow[-NaBr]{NaI}$$

$$\underset{\text{1–Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$

OR

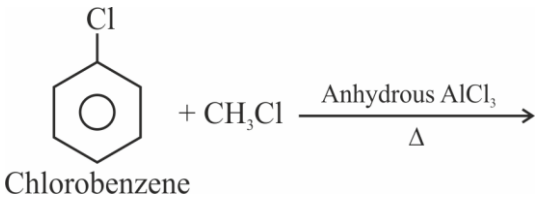
(iii) (a) $CH_3-CH_2-\overset{H}{\overset{|}{C}}-CH_3 \xrightarrow[-KBr,\,-H_2O]{\text{Alcoholic KOH}}$

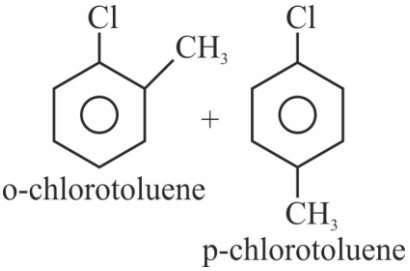
$$CH_3-\overset{H}{\overset{|}{C}}=C-CH_3$$

$$\underset{H}{|}$$

But-2-ene [major product]

(b) Alkylation of chlorobenzene





(major product)

30. (i) The correct increasing order of pK_b values in aqueous solution is :

$(C_2H_5)_2NH < (C_2H_5)_3N < C_2H_5NH_2$

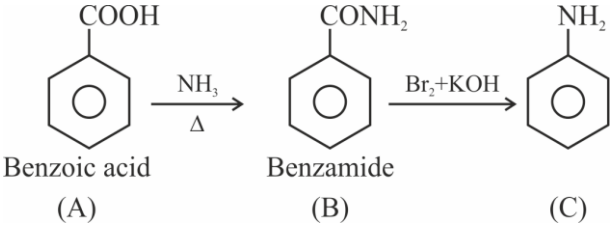
(2^o) (3^o) (1^o)

(ii) In the strongly acidic medium (like nitric acid), aniline is protonated to form the anilinium ion which is meta directing. That is why beside the ortho and para derivatives, significant amount of meta derivative (47%) is also formed.

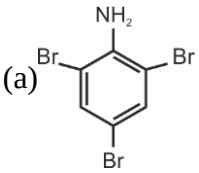
(iii) When benzaldehyde reacts with aqueous ammonia, it forms benzylideneamine (compound B), which is also known as benzaldehyde ammonia or phenylmethanamine. Upon heating benzylideneamine with Br, and aqueous KOH, it undergoes the Hofmann degradation reaction to form aniline (compound 'C') with the formula C_6H_7N.

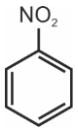
So, the structures are:

- A: Benzaldehyde (C_6H_5CHO)
- B: Benzylideneamine ($C_6H_5CH=NH$)
- C: Aniline ($C_6H_5NH_2$)



OR

(a) 

(b) 

31. (a) (i) $E_{cell} = E^0_{cell}-\frac{0.059}{n}\log\frac{[\text{oxidation}]}{[\text{reduction}]}$

Here, $2Al\rightarrow 2Al^{3+}+6e^-$

$3Ni^{2+}+6e^-\rightarrow 3Ni$

$E^0_{Cell}=E^0_{Cathode}-E^0_{Anode}$

$= -0.25 - (-1.66)$

$= -0.25 + 1.66$

$= 1.41$ V

So, $E_{cell} = 1.41 - \frac{0.059}{n}\log\frac{(0.001)^2}{(0.1)^3}$

$E_{cell} = 1.41 - \frac{0.059}{6}\log 10^{-3}$

$= 1.41 - 0.0098\,(-3)\log 10$

$= 1.41 + 0.0294$ [$\because \log 10 = 1$]

$= 1.4396$ V

(ii) For weak electrolytes, the degree of dissociation is very low at higher concentrations. As the concentration approaches zero, the degree of dissociation increases, making it impossible to extrapolate the A vs C curve like strong electrolytes. The curve for weak electrolytes is not linear and does not intersect the y-axis.

OR

(b) Given : $\Lambda_m^0\left(NH_4^+\right) = 73.8 Scm^2mol^{-1}$

$\Lambda_m^0\left(Cl^-\right) = 76.2 Scm^2mol^{-1}$

Conductivity of 0.1 M $NH_4Cl = 12.9 \times 10^{-2} S\ cm^{-1}$

$\Lambda_m = \frac{\text{Conductivity}}{\text{Concentration}} = \frac{12.9\times10^{-2}}{0.1} = 129 Scm^2mol^{-1}$

$\Lambda_m^0\left(NH_4Cl\right) = \Lambda_m^0\left(NH_4^+\right) + \Lambda_m^0\left(Cl^-\right)$

$= 73.8 + 76.2 = 150 Scm^2mol^{-1}$

Degree of dissociation

$(\alpha): \alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{129}{150} = 0.86$

(ii) Using Nernst equation:

$cell = E_{cell}^0 - \frac{0.059}{n}\log\frac{1}{\left[Zn^{2+}\right]}$

$E_{cell} = -0.76V - \frac{0.059}{2}\log\frac{1}{0.1}$

$E_{cell} = -0.76V - 0.0295 \log 10$

$E_{cell} = -0.76V - 0.0295 \times 1$

$E_{cell} = -0.76V - 0.0295V$

$E_{cell} = -0.7895V$.

32. (a) (1) Zn^{2+} salts are colourless because Zn^{3+} has a completely filled d-orbital (d^{10} configuration) and does not exhibit d-d transitions, while Ni^{2+} has partially filled d-orbitals (d^8 configuration) allowing d-d transitions which give colour.

(2) Cr^{2+} is a strong reducing agent because it readily gets oxidized to Cr^{3+}, which is more stable due to a half-filled t_{2g} configuration in the octahedral crystal field.

(3) Transition metals and their compounds show catalytic activities due to their ability to adopt multiple oxidation states and form complexes, providing active sites for the reaction.

(4) (i) $2MnO_4^- + 10I^- + 16H^+ \rightarrow$

$2Mn^{2+} + 5I_2 + 8H_2O$

(ii) With Fe^{++} ion

$2MnO_4^- + 16H^+ + 10Fe^{2+} \rightarrow$

$2Mn^{2+} + 8H_2O + 10Fe^{3+}$

(b) (i) CrO_4^{2-}, MnO_4^-

(ii) It convert $K_2Cr_2O_7$ into K_2CrO_4

$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$

(iii) Cu^+ is not stable in aqueous solution because it disproportionates to Cu and

$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

(iv) Cerium (Ce).

(v) Copper (Cu)

33. (a) (i) The boiling point of a solution is elevated when a solute is added due to the phenomenon known as boiling point elevation, which is directly proportional to the number of solute particles in the solution. NaCl is an electrolyte and dissociates into two ions, Na" and Cl in solution, thereby increasing the number of solute particles. On the other hand, glucose is a non-electrolyte and does not dissociate in solution. As a result, the I M NaCl solution has more solute particles than the 1 M glucose solution, leading to a higher boiling point for the NaCl solution.

(ii) The relative lowering of vapour pressure is given by:

$$\frac{\Delta P}{P^0} = \frac{n_B}{n_A} = \frac{\frac{W_X}{M_X}}{\frac{W_{benzene}}{M_{benzene}}}$$

Where:

Substituting the values:

$$0.1 = \frac{\frac{W_X}{50}}{\frac{78}{78}} = \frac{W_X}{50}$$

$W_X = 50 \times 0.1 = 5g$

So, the mass of solute X dissolved is 5 g.

(iii) $\Delta T_b = i \times K_b \times m$

Where:

$$\Delta T_b = i \times k_b \times \frac{w_b}{m_b} \times \frac{1}{w_a(\text{in kg})}$$

ΔT_b = Boiling point elevation

i = Van't Hoff factor (i = 3 for $MgCl_2$)

M = molar mass of solute = 95g

W = weight of solvent in kg = 0.2 kg

$$\Delta T_b = 3 \times 0.512 \times \frac{12}{95 \times 0.2}$$

$$\Delta T_b = 3 \times 0.512 \times \frac{10}{19}$$

$\Delta T_b \approx 0.808K$

Thus, the boiling point elevation is approximately 0.808 K.

(b) The Van't Hoff factor (i) for a solute is defined as the ratio of the actual number of particles in solution after dissociation or association to the number of formula units initially dissolved in solution. For ethanoic acid (CH_3COOH) in benzene, it dimerizes to form (CH_3COOH), due to hydrogen bonding. Therefore, instead of dissociating into ions, two molecules of ethanoic acid associate to form one dimer molecule, effectively reducing the number of particles by half. This is why the Van't Hoff factor (i) is close to 0.5.

(ii) Determine the osmotic pressure of a solution prepared by dissolving 2.32×10^{-2} g of K_2SO_4 in 2 L of solution at 25ºC assuming that K_2SO_4 is completely dissociated.

Fint, calculate the mamber of moles of K_2SO_4

$$n = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{2.32 \times 10^{-2}}{174} = 1.33 \times 10^{-4} \text{mol}$$

Since K_2SO_4 dissociates completely into 3 ions ($2K^+$ and SO_4^{2-}), the Van't Hoff factor, i, is 3.

The osmotic pressure is given by:

$$\pi = i \times \frac{n}{V} \times R \times T$$

Substituting the values

$$\pi = 3 \times \frac{1.33 \times 10^{-4}}{2} \times 0.0821 \times 298$$

$\pi = 3 \times 6.65 \times 24.4758$

$\pi \approx 0.0049$atm

Thus, the osmotic pressure of the solution is approximately 0.0049 atm.

(iii) The molar mass of the Sulphur molecule is:

$M = x \times 32g\ mol^{-1}$

Using the freezing point depression formula:

$$\Delta T_b = i \times K_b \times m$$

$$\Delta T_f = i \times k_f \times \frac{w_b}{m_b} \times \frac{1000}{w_a(\text{in g})}$$

Substituting the values

$$0.512 = 5.12 \times \frac{25.6}{x \times 32} \times \frac{1000}{1000}$$

$$\frac{0.512}{5.12} = \frac{25.6}{32x}$$

$$0.1 = \frac{25.6}{32x} \qquad x = \frac{25.6}{3.2} = 8$$

Thus, the formula of Sulphur is S_8.