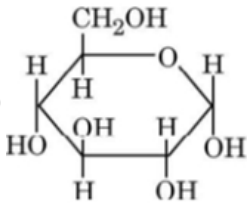
Section A

1. **(a)** propyl chloride with KCN

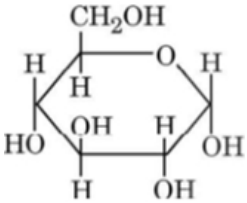
   Explanation:

   Butanenitrile can be prepared by heating propyl chloride with KCN.

2. **(a)**



   Explanation:



   represents α-D-glucose

3. **(c)** nucleophilic addition

   Explanation:

   In the treatment of cyanide or nitriles with aldehyde or ketone, there is the formation of aldehyde or ketone cyanohydrin. This is a nucleophilic addition reaction

4. **(c)** A - Methanol, B - Potassium formate

   Explanation:

   A - Methanol, B - Potassium formate

5. **(c)** 2

   Explanation:

   For 2nd order reaction, the half-life is inversely related to the concentration of the reactant.

   $t_{1/2}$ for second order reaction $\alpha \frac{1}{[R]}$

6. **(c)** (a) - (iii), (b) - (iv), (c) - (ii), (d) - (i)

   Explanation:

   (a) - (iii), (b) - (iv), (c) - (ii), (d) - (i)

7. **(c)** $C_6H_5CH(C_6H_5)Br$

   Explanation:

   $C_6H_5CH(C_6H_5)^+$ carbocation formed is more stable.

8. **(d)** Vitamin B_{12}

Explanation:

Deficiency of vitamin B_{12} (cyanocobalamin) causes the disease pernicious anaemia.

9.

(b) $\frac{2.303}{k}\log 4$

Explanation:

For a first order reaction,

$t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{k}\log\frac{a}{\frac{a}{4}} = \frac{2.303}{k}\log 4$

10. **(a)** Butan-2-ol

Explanation:

$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[KMnO_4]{alk} \underset{But\tan one}{CH_3CH_2COCH_3}$ Butan-2-ol converted to butanone

$But\tan -2-ol$

11.

(b) m – Chlorophenol

Explanation:

In cases of halogen derivatives of phenols or aniline or benzoic acid etc, it is very helpful to understand that all halogens, when attached to benzene ring, exerts -I as well as +R effect.

In case of Cl, Br and I, the +R effect has almost no effect on reactivity, acidic character or basic character of the benzene ring. It is due to very less effective overlapping involving 2p of carbon and 3p or 4p or 5p of halogen.

Hence, only -I effect becomes the deciding factor, which is most dominant from ortho-position and least effective from para-position. So m chlorophenol is most acidic.

12.

(b) C_6H_5NC

Explanation:

C_6H_5NC

13.

(b) Both A and R are true but R is not the correct explanation of A.

Explanation:

Oils float on water due to low specific gravity.

14. **(a)** Both (A) and (R) are true and (R) is the correct explanation of (A).

Explanation:

Both (A) and (R) are true and (R) is the correct explanation of (A).

15.

(c) Assertion (A) is true, but Reason (R) is false.

Explanation:

C – Cl bond is more ionic than C – I bond because of the greater difference in the electronegativities of C and Cl as compared to that of carbon and iodine. Therefore, C – Cl bond is stronger than the C – I bond.

16. **(a)** Both A and R are true and R is the correct explanation of A.

Explanation:

p-Nitrophenol is more acidic than phenol because the nitro group stabilizes phenoxide ion by dispersal of negative charge.

Section B

17. $\Lambda^{\circ}_{m(CaC_2)} = \Lambda^{\circ}_{m\left(Ca^{2+}\right)} + 2\Lambda^{\circ}_{m\left(Cr^{-}\right)}$

= 119 + (2 × 76.3) = 271.6 S cm^2 mol^{-1}

$\Lambda^{\circ}_{m(MgSO_4)} = \Lambda^{\circ}_{m(Mg^{2+})} + 2\Lambda^{\circ}_{m(SO_4^{2-})}$

= 106 + 160 = 266 S cm^2 mol^{-1}

OR

$Al^{3+} + 3e^- \rightarrow Al$

27 gram of Al require electricity = 3F

40 gram of Al require electricity $= \frac{3F}{27} \times 40$ = 4.44 F

18. Osmotic pressure (π) = $\frac{W \times R \times T}{M \times V}$

W = 5 gm, R = 0·0821 L atm K^{-1} mol^{-1}

V(Volume in litres) = $\frac{100}{1000}$

= 0.1 litres, M = 60 gm/mole, T = 300 K

$\pi = \frac{5 \times 0.0821 \times 300}{60 \times 0.1}$

Osmotic pressure at 300K = 20.525 atm

19. Chromium Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level. On the other hand, the change from (Manganese) Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

20. Answer the following:

(i) $t_{1/2} = \frac{0.693}{k}$

k = $\frac{0.693}{60}$ min^{-1}

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

$\frac{0.693}{60} = \frac{2.303}{t} \log \frac{100}{10}$

t = $\frac{2.303 \times 60}{0.693}$ min

t = 199.3 min

(ii)

Order of Reaction	**Unit of k**
1. Zero order reaction	$mol\,L^{-1}s^{-1}$
2. First order reaction	s^{-1}
3. Second order	$mol^{-1}\,Ls^{-1}$
4. n^{th} order reaction	$(mol/\,L)^{1-n}s^{-1}$

21. Methanal to Ethanal

$$H-CHO \;+\; CH_3MgBr \;\rightarrow H- \underset{\displaystyle H}{\overset{\displaystyle OMgBr}{\overset{|}{\underset{|}{C}}}} -CH_3 \xrightarrow{H^+/H_2O} CH_3-CHO$$

Section C

22. Oxidation of ferrous ion means:

$Fe^{2+} \rightarrow Fe^{3+} + e^-$; $E^0_{Fe^{3+}/Fe^{2+}} = 0.77V$

Any substance in which standard electrode potential is more than that of Fe^{+3}/F^{+2} can oxidize ferrous ions.

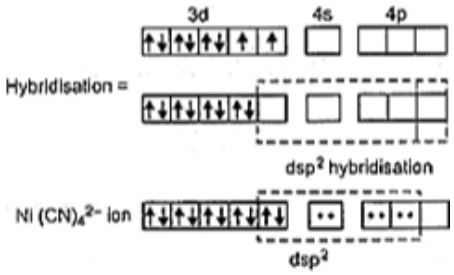
The EMF of the substance whose reduction potentials greater than 0.77v will oxidized ferrous ion. For example Br_2, Cl_2, and F_2.

23. a. On the basis of crystal field theory, for a d^4 ion, if $\Delta_0 < P$, then the complex is a high spin complex formed by the association of weak field ligands with the metal ion. As a result, the fourth electron enters one of the e_g orbitals, thereby, exhibiting the electronic configuration $t^3_{2g}e^1_g$.

b. Ni atom (z = 28)

E.C of Ni. = $[Ar]4s^2 3d^8$

E.C. of Ni^{2+} = $[Ar]4s^0 3d^8$

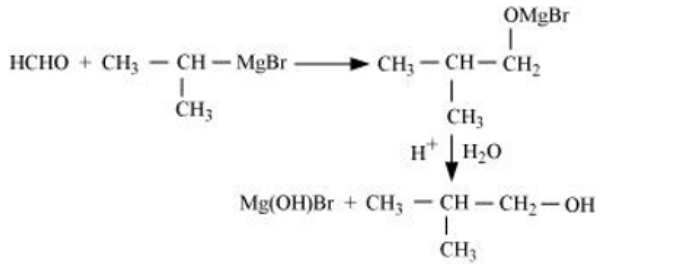


It is diamagnetic, due to the absence of unpaired electrons.

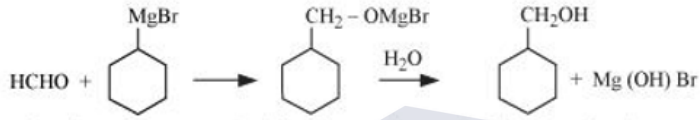
Shape - square planar.

c. $[CoCl_2(en)_2]$

24. i.



ii.



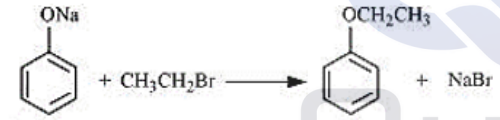
Methanal — Cyclohexylmagnesium bromide — Cyclohexylmethanol

OR

i. $CH_3CH_2CHONa + CH_3CH_2CH_2Br \rightarrow C_2H_5CH_2 - O - CH_2C_2H_5 + NaBr$

Sodium propoxide — I - Bromopropane — I - Propoxypropane

ii.



Sodium phenoxide — Bromoethane — Ethoxybenzene

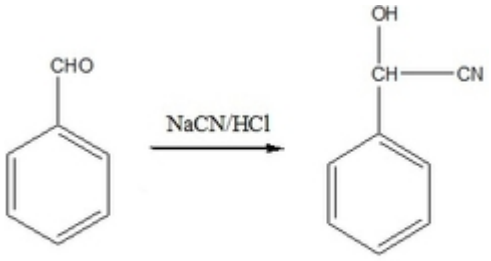
iii.

Sodium 2 – methyl – 2 – propoxide — Bromomethane — 2 – methoxy – 2 – methylpropane

iv. $CH_3CH_2 - ONa + CH_3 - Br \rightarrow CH_3CH_2 - O - CH_3 + NaBr$

Sodium ethoxide — Bromomethane — I - Methoxyethane

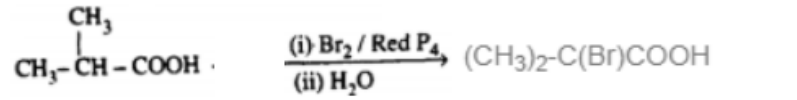
25. i.



Benzaldehyde — Benzaldehyde Cynohydrin

ii. $2CH_3 - \overset{O}{\overset{\|}{C}} - Cl + (C_6H_5CH_2)_2Cd \longrightarrow 2CH_3 - \overset{O}{\overset{\|}{C}} - CH_2C_6H_5 + CdCl_2$

Acetyl chloride — Dibenzyl cadmium — Benzyl methyl ketone

iii. 

2-methyl propanoic acid 2-methyl-2-bromo propanoic acid

26. It is used as reference electrode. Its electrode potential is taken as 0.00 volt. Hydrogen electrode consists of platinum wire coated with finely divided platinum black containing pure hydrogen gas at 1 atm and solution of HCl (1 M) so as to maintain equilibrium between H^+ ions and H_2(g).

At cathode

$2H^+ + 2e \rightarrow H_2$

At anode

$H_2 \rightarrow 2H^{2+} + 2e^-$

significance: In the measurement of electrode potential.

Benzyl chloride (1°) 1° carbocation

27.

Chlorodiphenylmethane 2° carbocation

Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH.

Now $C_6H_5CH_2Cl$ forms $1^\circ-$ carbocation, while $C_6H_5CHClC_6H_5$ forms $2^\circ-$ carbocation, which is more stable than $1^\circ-$ carbocation. Hence, $C_6H_5CHClC_6H_5$ is hydrolyzed more easily than $C_6H_5CH_2Cl$ by aqueous KOH.

28. Let the concentration of the reactant be [A] = a

Rate of reaction, $R = k[A]^2 = ka^2$

a. If the concentration of the reactant is doubled, i.e. [A] = 2a, then the rate of the reaction would be

$R' = k(2a)^2 = 4ka^2$

= 4R

Therefore, the rate of the reaction would increase by 4 times.

b. If the concentration of the reactant is reduced to half, i.e., $[A] = \frac{1}{2}a$ then the rate of the reaction would be $R' = k\left(\frac{1}{2}a\right)^2$

$= \frac{1}{4}ka^2 = \frac{1}{4}R$

Therefore, the rate of the reaction would be reduced to $\frac{1}{4}th$.

Section D

29. i. It is because they contain 'Chiral' carbon atoms.

ii. Aspartic acid and Glutamic acid.

iii. Haemoglobin.

OR

Glycerol and fatty acids.

30. i. Excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds.

ii. Impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

iii. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis.

OR

Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution.

Section E

31. Attempt any five of the following:

(i) Mischmetall is an alloy which consists of a Lanthanoid metal (95%) and iron(5%) and traces of S, C, Ca & Al. A good amount of this alloy is used in magnesium based alloy to produce bullets, shell and lighter Flint.

(ii) When the particular oxidation state becomes less stable relative to the other oxidation states, one lower and one higher, it is said to undergo a disproportionation reaction.

For example, $3Mn^{VI}O_4^{2-} + 4\ H^+ \longrightarrow 2\ Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$

(iii) Fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air to form sodium chromate

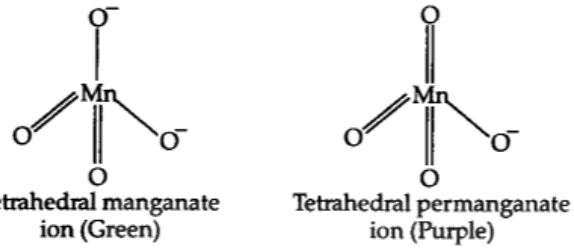
$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$

On acidification of Sodium chromate with sulphuric acid to form sodium dichromate

$2\ Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$

(iv) Due to comparable energies of 5f, 6d and 75 levels members of actinoid series exhibit a large number of oxidation states.

(v)



Tetrahedral manganate ion (Green) | Tetrahedral permanganate ion (Purple)

(vi) +2 and +4 oxidation states are due to high stabilities of f^0, f^7 and f^{14} configuration.

(vii) La^{3+} (lanthanum) have $4f^0$ and Lu^{3+} (lutetium) have $4f^{14}$ configuration. Because of the absence of unpaired electrons, these ions impart no colour to the solution.

32. a. i. Since the compound C of molecular formula C_6H_7N is formed B on treatment with Br_2 and KOH (Hoffmann bromamide reaction), therefore, the compound 'B' must be an amide and 'C' must be an amine. The only aromatic amine having molecular formula C_6H_7N is $C_6H_5NH_2$ (aniline).

ii. Since 'C' is aniline, the amide from which is formed by must be benzamide ($C_6H_5CONH_2$).

$$\underset{Aniline\ (C)}{C_6H_5NH_2} \xleftarrow{Br_2,\ KOH} \underset{Benzamide\ (B)}{C_6H_5CONH_2}$$

Thus, B is benzamide.

iii. Since B is formed from A with aqueous ammonia and heating, therefore, compound 'A' must be benzoic acid.

$$\underset{Benzoic\ acid\ (A)}{C_6H_5COOH} \xrightarrow[Heat]{aq.NH_3} \underset{Benzamide\ (B)}{C_6H_5CONH_2}$$

Thus, A = C_6H_5COOH, B = $C_6H_5CONH_2$, C = $C_6H_5NH_2$.

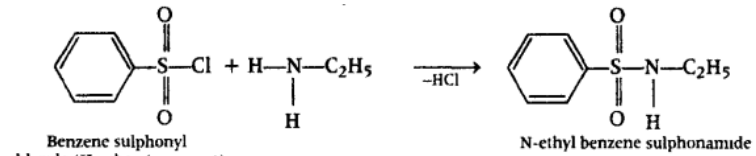
b. i. $C_6H_5NH_2 + CHCl_3 + 3\underset{(alc)}{KOH} \rightarrow \underset{Phenyl\ isocyanide}{C_6H_5NC} + 3KCl + 3H_2O$

ii. $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow \underset{Benzene}{C_6H_6} + N_2 + H_3PO_3 + HCl$

OR

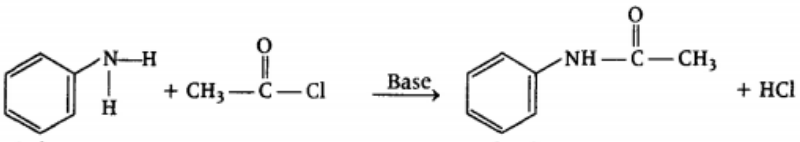
i. $\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HNO_2 \xrightarrow{0^\circ C} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + N_2 + H_2O$

ii.



Benzene sulphonyl chloride (Hinsberg's reagent) | N-ethyl benzene sulphonamide

iii.



Aniline | N-phenyl ethanamide (Acetanilide)

33. Molar mass of benzene $(C_6H_6) = (6 \times 12) + (6 \times 1)$

$= 78\ g\ mol^{-1}$

Molar mass of toluene $(C_6H_5CH_3) = (7 \times 12) + (8 \times 1)$
= $92\, g\, mol^{-1}$
Now, no. of moles present in 80 g of benzene = $\frac{80}{78} mol$
= 1.026 mol
And, no. of moles present in 100 g of toluene = $\frac{100}{92} mol$
=1.087 mol
Therefore, Mole fraction of benzene, $x_b = \frac{1.026}{1.025+1.087}$
= 0.486
And, mole fraction of toluene, $x_t = 1 - 0.486$ = 0.514
It is given that vapour pressure of pure benzene, $p_b^0 = 50.71\, mm\, Hg$
And, vapour pressure of pure toluene, $p_1^0 = 32.06\, mm\, Hg$
Therefore, partial vapour pressure of benzene, $p_b = x_b \times p_b$
$= 0.486 \times 50.71$
= 24.645 mm Hg
And, partial vapour pressure of toluene, $p_1 = x_t \times p_t$
$= 0.514 \times 32.06$
= 16.479 mm Hg
Hence, mole fraction of benzene in vapour phase is given by:
$\frac{p_b}{p_b+p_t}$
$= \frac{24.645}{24.645+16.479}$
$= \frac{24.645}{41.124}$
= 0.599

OR

a. The order of depression in freezing point is $CH_3COOH < Cl_3C - COOH < F_3C - COOH$. As fluorine is most electronegative so causes highest electron withdrawing inductive effect (-I effect). Consequently, it is strongest acid. Hence CF_3COOH ionises to the largest extent while acetic acid ionises to minimum extent. As we know greater the ions produced, more will be depression in freezing point. Hence, the depression in freezing point is maximum for the fluoroacetic acid and minimum for acetic acid.

b. Given, $w_A = 65.0g$
$\Delta T_f = 7.5^0\ C$
$K_f = 1.86^0\ C/m$
i = 1.87
$M_B = 58.5\, g\, mol^{-1}$
As we know,
$\Delta T_f = \frac{i \times K_f \times w_B \times 1000}{M_2 \times w_A}$
$\Rightarrow\ w_B = \frac{\Delta T_f \times M_B \times w_A}{i \times K_f \times 1000}$
$w_B = \frac{7.5^\circ C \times 58.5g\ mol^{-1} \times 65g}{1.87 \times 1.86^\circ C/m \times 1000g\ kg^{-1}}$
= 8.199 g.