SOLUTIONS

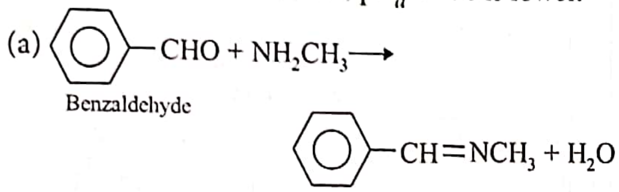
1. At dynamic equilibrium,
Rate of formation of complex = Rate of disappearance of complex

$(1.45 \times 10^{13})[Fe^{2+}][dipy]^3 = (1.22 \times 10^{-4})[Fe(dipy)_3]^{2+}$

$\therefore\ k = \frac{[Fe(dipy)_3]^{2+}}{[Fe^{2+}][dipy]^3} = \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}$

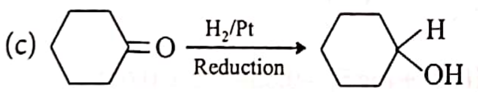
2. (a) Due to presence of electron withdrawing group (—COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.
(b) Due to presence of strong electron withdrawing group ($—NO_2$), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore, pK_a value is lower.

3. (a)



(b) $CH_3CH_2CHO + \underset{\displaystyle CH_3}{\underset{|}{CH_2}} - CHO \xrightarrow[\text{Aldol condensation}]{NaOH} CH_3 - CH_2\overset{\displaystyle OH}{\overset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{C}HCHO}$

(c)



4. (a) Primary amine
(b) Primary amine
(c) Tertiary amine

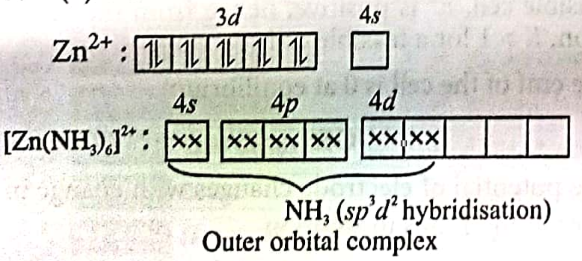
OR

(a) $CH_3Cl \xrightarrow{KCN} \underset{(A)}{CH_3CN}$

(b) $CH_3CN \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2}$

(c) $CH_3CH_2NH_2 \xrightarrow{CHCl_3 + \text{alc. } KOH} \underset{(C)}{CH_3CH_2NC}$

5. (a) $Zn^{2+} \rightarrow 3d^{10}\,4s^0$



In other cases NH_3 being strong field ligand causes pairing of electrons and the resulting complexes will be inner orbital. But in case of Zn, their is no availability of inner *d*-orbital due to fully filled *d*-orbital.

(b) Oxidation state of Ni in $[Ni(H_2O)_6]^{2+} = +2$
$Ni^{2+}\ (Z = 28) \rightarrow 3d^8$
Since, H_2O is a weak field ligand, electrons remain unpaired hence, the compound is paramagnetic.

OR

(a) $[Fe(H_2O)_6]^{2+} < [Fe(CN)_2(H_2O)_4] < [Fe(CN)_4(H_2O)_2]^{2-}$

The value of Δ_o for mixed ligands depends on the additive contributions of the ligand strength. Since CN^- has greater ligand strength than H_2O, the strength increases as the number of CN^- ions increases.

(b) $\underset{(n=0)}{[Cu(H_2O)_4]^+} < \underset{(n=1)}{[Cu(NH_3)_4]^{2+}} < \underset{(n=3)}{[CoF_6]^{3-}}$

6. The amount of gas adsorbed by a solid depends on the nature of gas. In general, more easily liquefiable gases (*i.e.*, higher critical temperature) are readily adsorbed as van der Waals' forces are stronger near the critical temperature.
More easily liquefiable gases, (*e.g.*, NH_3, CO_2) are readily adsorbed, as van der Waals forces are stronger near the critical temperatures. So, adsorption of CO_2 will be highest.

7. For a first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.4 \times 60 \times 60} = 8.02 \times 10^{-5}\ s^{-1}$$

(a) Now using the expression

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

$a = 10$ g; $t = 9.6$ hr $= 9.6 \times 60 \times 60$ s; $k = 8.02 \times 10^{-5}\ s^{-1}$

$$8.02 \times 10^{-5} = \frac{2.303}{9.6 \times 60 \times 60}\log\frac{10}{a-x}$$

$$\log\frac{10}{a-x} = \frac{8.02 \times 10^{-5} \times 9.6 \times 60 \times 60}{2.303}$$

$$\log\frac{10}{a-x} = \frac{2.77171}{2.303} \Rightarrow \frac{10}{a-x} = 15.9$$

$$\underset{\text{(amount left)}}{a-x} = \frac{10}{15.9} = 0.628\ \text{g}$$

(b) $t = \frac{2.303}{k}\log\frac{a}{a-x}$

$$t = \frac{2.303}{8.02 \times 10^{-5}}\log\left(\frac{5.0 \times 10^{10}}{1.0 \times 10^{8}}\right) = \frac{2.303 \times 2.698}{8.02 \times 10^{-5}}$$

$= 77503$ s $= 21.52$ hr

8. (a) $CH_3CH_2CN \xrightarrow[\text{Partial hydrolysis}]{H^+ \text{ or } OH^-} CH_3CH_2-\overset{\overset{O}{||}}{C}-NH_2$

Ethyl cyanide → Propanamide

Propanamide $\xrightarrow{Br_2-NaOH}$ $CH_3CH_2NH_2$ (Ethylamine)

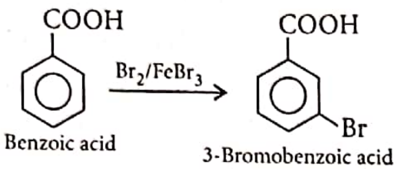
$CH_3CH_2OH \xleftarrow[-N_2, -H_2O]{HONO} CH_3CH_2NH_2$

Ethanol ← Ethylamine

Ethanol $\xrightarrow[\text{Oxidation}]{K_2Cr_2O_7/H_2SO_4}$ CH_3COOH (Ethanoic acid)

(b) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Oxidation}]{K_2Cr_2O_7/H_2SO_4} CH_3CH_2CH_2COOH$

Butan-1-ol → Butanoic acid

(c) 

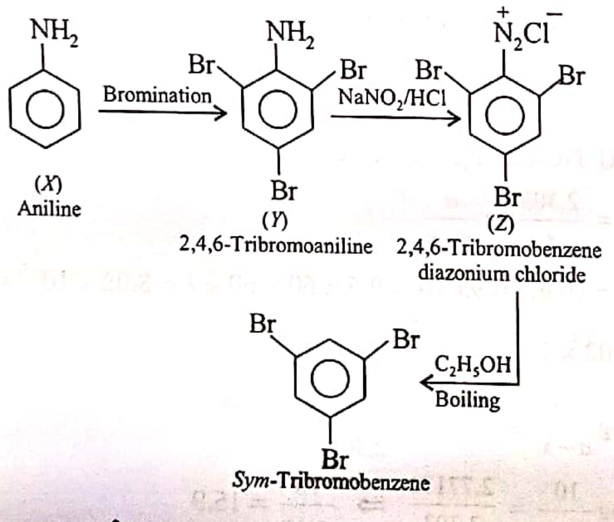
9. (a) $CH_3CH_2Br \xrightarrow{KCN} \underset{(A)}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2CH_2NH_2}$

$\underset{(C)}{CH_3CH_2CH_2OH} \xleftarrow[HNO_2]{273\text{ K}} \underset{(B)}{CH_3CH_2CH_2NH_2}$

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2 + NaOH} \underset{(B)}{CH_3NH_2}$

$\underset{(C)}{CH_3NC} \xleftarrow{CHCl_3 + NaOH} \underset{(B)}{CH_3NH_2}$

OR



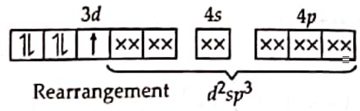
10. (a) Cr^{2+} is reducing since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

(b) Cu^+ is unstable in aqueous solution. In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

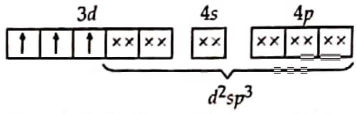
$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

(c) Mn^{3+} is a strong oxidising agent because electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily.

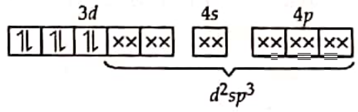
11. (a) $[Mn(CN)_6]^{4-}$:



(b) $[Cr(NH_3)_6]^{3+}$:



(c) $[Co(NH_3)_6]^{3+}$:



OR

	Complex	Central metal ion atom	Hybridisation of metal ion involved	Geometry of complex	Magnetic behaviour
(a)	$[Cr(NH_3)_4Cl_2]Cl$	Cr^{3+}	d^2sp^3	Octahedral	Paramagnetic
(b)	$[Co(en)_3]Cl_3$	Co^{3+}	d^2sp^3	Octahedral	Diamagnetic
(c)	$K_2[Ni(CN)_4]$	Ni^{2+}	dsp^2	Square planar	Diamagnetic

12. (a) $\underset{(1\text{ M})}{M} \longrightarrow \underset{(0.05\text{ M})}{M^+} + e^-$

For concentration cell, $E_{cell} = -\frac{0.059}{1}\log\frac{0.05}{1}$

$E_{cell} = -\frac{0.059}{1}\log(5\times10^{-2})$

$E_{cell} = -\frac{0.059}{1}[(-2)+\log 5]\ -0.059(-2+0.698)$

$= -0.059(-1.302) = 0.0768$ mV

(b) $\frac{E_1}{E_2} = \frac{\log 0.05}{\log 0.0025}$

$\frac{E_1}{E_2} = \frac{\log 5\times10^{-2}}{\log 25\times10^{-4}}$

$E_1 = 0.0768$ mV

$\frac{0.0768}{E_2} = \frac{-1.3}{-2.6} = \frac{1}{2}$ or $E_2 = 154$ mV

(c) $K = \text{antilog}\left(\frac{nE^\circ}{0.0591}\right)$

For feasible cell, E° is positive, hence from the above equation, $K > 1$ for a feasible cell reaction.

(d) The emf of the cell is 0 at equilibrium.

OR

Yes, the potential of electrode changes with change in concentration of ions in solution.

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