SOLUTIONS

1. (a) Butanone < Propanone < Propanal < Ethanal
   (b) Benzaldehyde < Propanaldehyde < Acetaldehyde < Formaldehyde
   (c) Benzophenone < Acetophenone < Acetone < Formaldehyde

2. $EMF = E^\circ_{cathode} - E^\circ_{anode} = 0.76 - 0.41 = 0.35$ V

3. The time taken for half of the reaction to complete, i.e., the time in which the concentration of a reactant is reduced to half of its original value is called half-life period of the reaction.

$t = t_{1/2}$ when $[R] = \dfrac{[R_0]}{2}$

(a) For zero order reaction rate constant is given by :

$k = \dfrac{[R]_0 - [R]}{t}$, At $t = t_{1/2}, [R] = \dfrac{[R]_0}{2}$

$k = \dfrac{[R]_0 - \dfrac{[R]_0}{2}}{t_{1/2}} \Rightarrow k = \dfrac{[R]_0}{2t_{1/2}} \Rightarrow t_{1/2} = \dfrac{[R]_0}{2k}$

In zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

(b) For first order reaction,

$k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$, At $t = t_{1/2}, [R] = \dfrac{[R]_0}{2}$

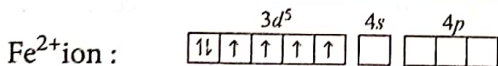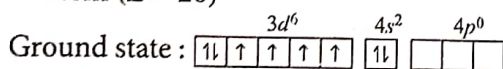$\therefore k = \dfrac{2.303}{t_{1/2}} \log \dfrac{[R]_0}{[R]_0/2}$ or, $t_{1/2} = \dfrac{2.303}{k} \log 2$

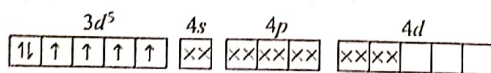$t_{1/2} = \dfrac{2.303 \times 0.3010}{k} \Rightarrow t_{1/2} = \dfrac{0.693}{k}$

In first order reaction, $t_{1/2}$ is independent of initial concentration.

4. (a) $[Fe(H_2O)_6]^{2+}$:
   Fe atom ($Z = 26$)

   Ground state :

   Fe^{2+} ion :

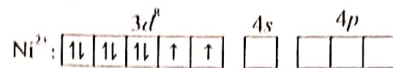

   $[Fe(H_2O)_6]^{2+}$:

   sp^3d^2 hybridisation
   six pairs of electrons
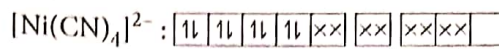   from six H_2O ligands
   (weak ligand)

   The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of four unpaired electrons.

Chemistry

(b) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration.
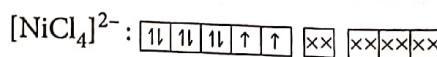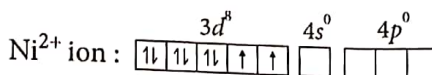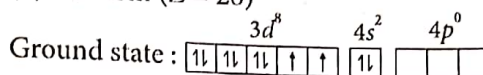

(In ground state)

$[Ni(CN)_4]^{2-}$:

dsp^2 hybridisation
four electrons pairs
donated by four
CN ions
(Strong ligand)

The complex ion has square planar geometry and is diamagnetic in nature.

OR

(a) Tetrachloridonickelate(II) ion
(b) Ni atom ($Z = 28$)

Ground state :

Ni^{2+} ion :

$[NiCl_4]^{2-}$:

sp^3 hybridisation
four pairs of electrons
from four Cl^- ligands
(weak ligands)

(c) The complex ion has tetrahedral geometry and is paramagnetic due to the presence of unpaired electrons.

5. (a) Transition metals form a large number of complex compounds due to following reasons :
   − Comparatively smaller size of metal ions.
   − High ionic charges.
   − Availability of d-orbitals for bond formation.

(b) Lowest oxidation compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas, the higher oxidation state of metal and compounds gets reduced to lower ones and hence are acidic in nature. e.g., MnO is basic whereas Mn_2O_7 is acidic.

(c) Much larger third ionisation energy of Mn(where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

OR

(a) Ti^{4+} has highest oxidation state among the given ions. Ti^{4+} has stable inert gas configuration and hence, most stable in aqueous solution.
On the other hand, V^{2+}, Mn^{3+}, Cr^{3+} have unstable electronic configuration and hence, are less stable.

(b) Due to presence of highest oxidation state of Ti, it acts as the strongest oxidising agent among the given ions.

(c) Due to absence of unpaired electron in Ti^{4+}, it is a colourless ion.

E.C. of Ti^{4+} : $[Ar]3d^0 4s^0$

6. (a) Due to reduction of NO_3^- in preference to H^+ ion. H^+ ion is not reduced to give H_2 gas.

(b) Higher the reduction potential, stronger is the oxidising agent.

(c) Iron coated with zinc does not get rusted even if cracks appear on the surface because Zn will take part in redox reaction not Fe as Zn is more reactive than Fe. If iron is coated with tin and cracks appear on the surface, Fe will take part in redox reaction because Sn is less reactive than Fe.

7. (a) H_2 decreases three times as fast as that of N_2 while NH_3 increases twice as fast as that of N_2 decreases.

Hence, Rate $= -\dfrac{1}{3}\dfrac{d[H_2]}{dt} = +\dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

(b) For zero order reaction rate constant

$= \dfrac{mol\ L^{-1}}{s} \times \dfrac{1}{(mol\ L^{-1})^0} = mol\ L^{-1}\ s^{-1}$

For first order, rate constant $= \dfrac{mol\ L^{-1}}{s} \times \dfrac{1}{mol\ L^{-1}} = s^{-1}$

8. (a) Pine oil is adsorbed on sulphide ore particles resulting in formation of emulsion and froth.

(b) In multimolecular colloids, the smaller particles aggregate and are held together by van der Waals' forces, e.g. sols of gold atoms and sulphur molecules.

(c) The method involves both dispersion and condensation. The intense heat of arc vapourises some of the metal which condenses under cold water.

9. Formula of the compound 'C' indicates it to be an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound 'B' so compound 'B' can be an amide. It is also indicated because 'B' is obtained from compound 'A' by reaction with ammonia following by heating. So compound 'A' could be an aromatic acid. Formula of compound 'C' shows that it is aniline, then 'B' is benzamide and compound 'A' is benzoic acid. The sequence of reactions can be written as follows :
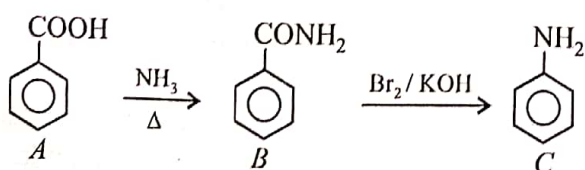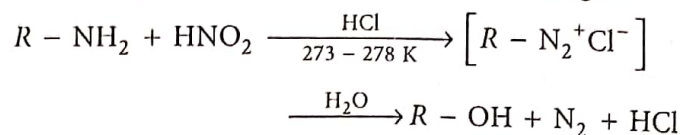

OR

(a) Aromatic primary amines react with nitrous acid to form diazonium salts.
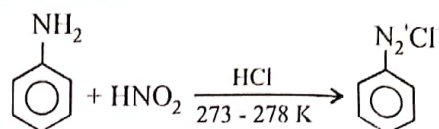
(b) Aliphatic primary amines also form diazonium salts on reaction with nitrous acid but they are unstable and decompose to give the corresponding alcohols as the major product with the evolution of nitrogen.
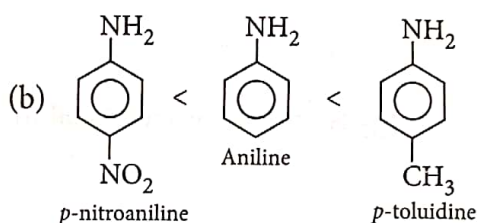
$R - NH_2 + HNO_2 \xrightarrow[273-278\ K]{HCl} \left[R - N_2^+ Cl^- \right]$

$\xrightarrow{H_2O} R - OH + N_2 + HCl$

10. (a) Potassium pentacyanonitrosylferrate(II)

(b) Pentaamminenitrocobalt(III) chloride

(c) Dibromido*bis*(ethane-1,2-diamine)chromium(III) bromide

11. (a) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(b)

Electron withdrawing group ($-NO_2$) on benzene ring decreases the basicity and electron donating group ($-CH_3$) on benzene ring increases the basicity of compound.

(c) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

$C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine, $C_6H_5CH_2NH_2$ since in aromatic amines lone pair of nitrogen is in conjugation with benzene ring. But due to $+I$ effect of $-CH_3$ group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$.

OR

(a) After acetylation of aniline, acetanilide is formed in which due to the presence of $-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$ group having $-I$ effect, electron density on N-atom decreases and hence, activation effect of aniline gets reduced.

(b) CH_3NH_2 is more basic than $C_6H_5NH_2$ because in aniline the lone pair of electrons on nitrogen are involved in resonance.

(c) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and

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is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta-*directing group. Hence, the incoming electrophile goes to *m*-position.

12. (a) It is an example of cross Cannizzaro reaction where aromatic aldehyde gets reduced to alcohol and aliphatic aldehyde gets oxidised to its sodium salt (both aldehydes must not contain any α-hydrogen).

(b) Benzaldehyde undergoes Cannizarro reaction while acetaldehyde undergoes Aldol condensation.

(c) Hydride transfer is the slowest step.

$$Ph-\overset{O}{\overset{||}{C}}-OH+ Ph-CH_2O^-$$

(d) C—C bond is not formed in Cannizzaro reaction while other reactions result in the formation of C—C bond.

OR

The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.

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