SOLUTIONS

1. All natural and artificial radioactive decay of unstable nuclei takes place by first order kinetics. **[1]**

$${}^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$

Hydrogenation of ethene and decomposition of N_2O_5 and N_2O are also the examples of first order reactions. **[1]**

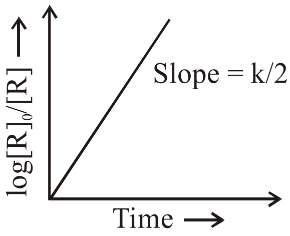
2. For first order reaction,

$$k = \frac{1}{t}\ln\frac{[R]_0}{[R]}$$

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

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

If we plot a graph between log $[R]_0$ / [R] vs t, we get a straight line with the slope = $\frac{k}{2.303}$ as shown below :



3. For first order reaction, **[1]**

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

and unit of k is s^{-1}.

4. Rate constant (k) = $\frac{0.693}{60\,\text{min}}$ **[1]**

$$= \frac{0.693}{(60 \times 60)} = 1.925 \times 10^{-4}\ s^{-1}$$

5. $[R]_0 = 100$, $[R] = 100 - 30 = 70$, $t = 40$ min. **[1]**

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = \frac{2.303}{40}\log\frac{100}{70}$$

$$= \frac{2.303}{40} \times 1.1548$$

$\therefore$ $k = 8.91 \times 10^{-3}\ \text{min}^{-1}$

6. Benzoyl peroxide. **[1]**

7. Roasting. **[1]**

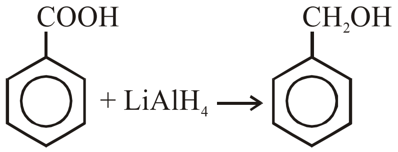
8. Ellingham diagram. **[1]**

9. Invert sugar. **[1]**

10. Addition reaction.

11. (a) Orlon (acrilan) is the commercial name of polyacrylonitrile. **[1]**

12. (d) Benzoic acid reacts with $LiA1H_4$ to give benzyl alcohol. **[1]**



[1]

13. (a) 1° amines have the highest boiling points due to the presence ot two H-atoms that would undergo hydrogen bonding to a greater extent as compared to 2° and 3° amines. **[1]**

14. (b) Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharide. Some common examples are starch, cellulose, glycogen, etc.

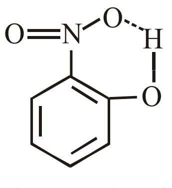
Polysaccharides are not sweet in taste, hence they are called non-sugars. They are classified as either reducing or non-reducing sugar. All those carbohydrates which reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are reducing sugars. **[1]**

15. (d) Exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting which cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. **[1]**

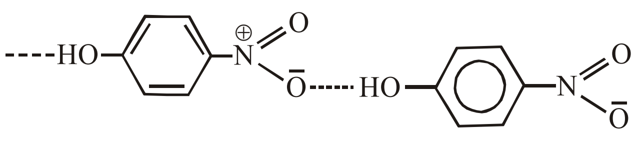
16. (a) In the presence of enzymes, substrate molecules can be attacked by the reagent effectively as the active sites of enzymes hold the substrate molecule in a suitable position. Therefore, both assertion and reason are correct and reason is the correct explanation of assertion. **[1]**

17. (a) Half and compleiely filled set of orbitals are relatively more stable. Thus, electronic configuration of Cr is $3d^5\ 4s^1$ instead of $3d^4$ and $4s^2$. The energy gap between the two sets (3d and 4s) of orbitals is small enough to prevent electron entering the 3d-orbitals. Similarly, in the case of Cu, the configuration is $3d^{10}\ 4s^1$ and not $3d^9\ 4s^2$. **[1]**

18. (d) o-nitrophenol is more volatile due to intramolecular hydrogen bonding, while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



o-nitrophenol (intramolecular H-bonding)



[1]

p-nitrophenol (intermolecular H-bonding)

19. (c) Carboxylate ion is more stable than phenoxide ion due to two equivalent resonating structures in which negative charge is at the O-atom. In phenoxide ion, negative charge is at the less electronegative carbon atom. **[1]**

20. (c) Synthetic polymers are not biodegradable as they are not degraded by enzymatic hydrolysis and environmental oxidation. Polymerisation does not induce toxic character in organic molecules. **[1]**

21. (i) Given that, Rate = k $[CH_3OCH_3]^{3/2}$

In this problem, pressure is in bar and time is in minutes. So, the unit of rate = bar min^{-1}

Also, unit of k = Unit of rate/unit of $[CH_3OCH_3]^{3/2}$

$\therefore$ Unit of k = bar min^{-1}/ $bar^{3/2}$ = $bar^{-1/2}$ min^{-1}. **[1]**

(ii) Yes, it is possible to have a negative activation energy value when rates of reaction decreases with increase in temperature. **[1]**

Or

Given, T_1, = 600 K, T_2 = 700 K

E_a =209kJ, k_1 =1.6×10^{-5} s^{-1}

As we know that,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad ....(i)$$

Putting the values in Eq. (i), we get

$$\log \frac{k_2}{1.6\times10^{-5}} = \frac{209\times10^{3.}}{2.303\times8.314}\left[\frac{700-600}{700\times600}\right]$$

$$= 10.9 \times \frac{100}{420000}\times1000$$

$$\log \frac{k_2}{1.6\times10^{-5}} = 2.599$$

$$\frac{k_2}{1.6\times10^{-5}} = \text{antilog } (2.599)$$

$k_2 = 397.2 \times 1.6 \times 10^{-5}$

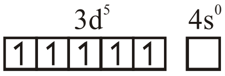
$= 635.52 \times 10^{-5}\ sec^{-1} = 6.35 \times 10^{-3}\ sec^{-1}$ **[2]**

22. **$[FeCN_6]^{3-}$** In this complex, Fe is present as Fe^{3+} .

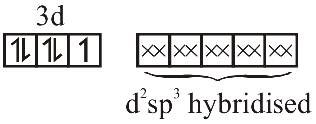
The electronic configuration of

Fe = [Ar] $3d^6$ $4s^2$

Ouler electronic configuration of Fe^{3+} = $3d^5$ $4s^0$

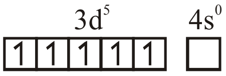
Fe^{3+} =


CN⁻ being a strong field ligand, pairs up the unpaired d-electrons. Thus, low spin complex is formed.

$[Fe(CN)_6]^{3-}$ =


[1]

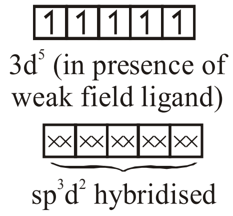
$[FeF_6]^{3-}$: In this complex, the oxidation state of Fe is + 3. Outer electronic configuration of Fe^{3+}= $3d^5 4s^0$

Fe^{3+} =


F^- is a weak field ligand, so no pairing occurs.

Thus, 3d-orbitals are not available to take part in bonding.

Thus, high spin complex is formed.

$[FeF_6]^{3-}$ = **[1]**


23. The resistance (R) of a conductor varies directly with length (l) and inversely with area of cross-section (A).

i.e. $R \propto \frac{l}{A}$ or $R = \rho \frac{l}{A}$

where , ρ = resistivity or $\rho = \frac{RA}{l}$

Conductivity (κ) is the reciprocal of resistivity (ρ).

So, $\kappa = \frac{1}{\rho} = \frac{1}{RA/l} = \frac{1}{RA} = \frac{1}{R}\left[\frac{l}{A}\right]$ **[1]**

$$\kappa = \frac{1}{R}\left[\frac{l}{A}\right] = \frac{1}{R}.G^*$$

Here, $G^* = \frac{l}{A}$ = cell constant

The molar conductivity of a solution is related to its conductivity by the following relation.

$\Lambda_m = \frac{\kappa \times 1000}{M}$ S cm^2 mol^{-1}

where, M = molarity

Thus, the cell constant, resistance of the solution in the cell and conductivity of the solution are related by the following expression :

$$\Lambda_m = \frac{\frac{G^*}{R} \times 1000}{M}$$ **[1]**

OR

Given Λ_m = 138.9 S cm^2 mol^{-1} **[1]**

Molarity, M = 1.5 M = 1.5 mol L^{-1}

κ = ?

we know that, $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$$138.96 \text{ S cm}^2 \text{ mol}^{-1} = \frac{\kappa \times 1000}{1.5 \text{ mol cm}^{-3}}$$

$$\kappa = \frac{138.9 \text{ S cm}^2 \text{ mol}^{-1} \times 1.5 \text{ mol cm}^{-3}}{1000}$$

$= 0.208 \text{ S cm}^{-1}$ **[2]**

24. **[4×½ =2]**

Coordination entities	Oxidation state of metal
(i) $[\overset{x}{Co}(\overset{0}{H_2O})(\overset{(-1)}{CN})(\overset{(0)}{en})_2]^{2+}$	+3
(ii) $[\overset{x}{Co}\overset{(-1)}{Br_2}(\overset{0}{en})_2]^{+}$	+3
(iii) $[\overset{(x)}{Pt}\overset{(-1)}{Cl_4}]^{2-}$	+2
(iv) $[\overset{(x)}{Cu}(\overset{(-1)}{CN})_4]^{3-}$	+1

25. (i) $SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$ **[1]**

(ii) $4FeS_2(s) + 11O_2(g) \longrightarrow 2F_eO_3(s) + 8SO_2(g)$ **[1]**

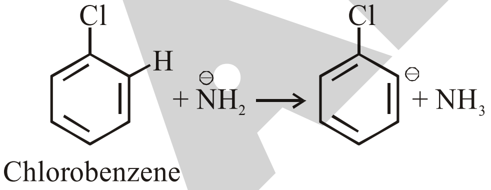
26. 2-chloroethanol is more acidic than ethanol. Due to –*I*-effect (electron withdrawing group) of the CI-atom electron density in O—H bond decreases. So, O— bond of 2-chloroethanol becomes weaker than O—- bond of ethanol.

Thus, 2-chloroethanol is more acidic than ethanol.

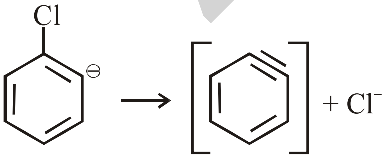
$Cl \leftarrow CH_2 \leftarrow CH_2 \leftarrow O \leftarrow H$

$CH_3 \leftarrow CH_2 \leftarrow O \leftarrow H$

27. **Step 1**

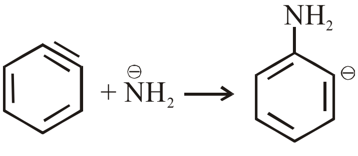


Step 2



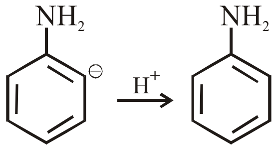
Benzyne intermediate
[Highly unstable]

Step 3



Carbanion

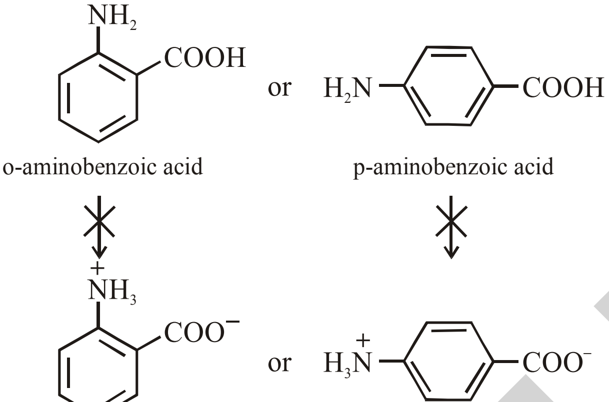
Step 4



Aniline

28. (i) In o- or p-arninobenzoic acids, the lone pair of electrons on the NH_2 group is donated towards the benzene ring. As a result, acidic character of –COOH group and basic character of $-NH_2$ group decreases. Therefore, the weakty acidic –COOH group cannot transfer H^+ ion to the weakly basic $-NH_2$ group.

Thus, o-or p-aminobenzoic acids do not exist as Zwitter ions.



However, in glycine, no such electron withdrawing benzene ring is present. As a result, –NH, group is sufficiently basic and, hence accepts a proton from –COOH group to form a Zwitter ion. **[2]**

$$\underset{\text{Glycine}}{H_2N-CH_2-COOH} \rightleftharpoons \underset{\text{Zwitter ion}}{H_3\overset{+}{N}-CH_2-COO^-}$$

(ii) Conjugated proteins on hydrolysis give a non-protein, portion in addition to the α-amino acids. This non-protein portion is called the prosthetic group. **[½]**

(iii) The sugar present in milk is lactose. Tne two monosaccharide units present in lactose are glucose and galactose.

29. The chemical substances which are used to relieve pain are called **analgesic medicines**. **[1]**

These are-classified into two. types :

(a) **Non-narcotic analgesias** These are non-addictive and effective in relieving skeletal pains, preventing heart attacks, reducing fever etc.

Example; Aspirin and paracetamol. **[1]**

(b) **Narcotic analgesics** These drugs produce steep, unconsciousness and convulsions. These are addictive drugs and are recommended for relieving post operative pain, cardiac pain and terminal cancer. Example, opiates. In poisonous doses, these produce stupor coma, convulsions and ultimately death. **[1]**

30. Given, $\pi = 0.75$ atm ; V = 2.5 L, i = 2.74 ;
T = 27°C = 27 + 273 = 300 K
R = 0.0821 L atm K^{-1} mol^{-1}

From, $\pi = iCRT = i\dfrac{n}{V}RT$ or $n = \dfrac{\pi \times V}{i \times R \times T}$

$$\therefore\ n = \frac{0.75 \text{atm} \times 2.5 \text{L}}{2.47 \times 0.0821 \text{L atm} K^{-1} \text{mol}^{-1} \times 300 \text{K}} = 0.0308 \text{ mol}$$

Molar mass of $CaCl_2$ = 40 + 2 × 35.5 = 111 g mol^{-1}
$\therefore$ Amount of $CaCl_2$ dissolved = n × M
= 0.0308 × 111 g
= 3.42 g **[1]**

Or

Among of K_2SO_4 dissolved = 25 mg = 0.025 g
Volume of solution = 2 L
T = 25°C = 25 + 273 = 298K
Molar mass of K_2SO_4 = 2 × 39 + 32 + 4 × 16
= 174 g mol^{-1} **[1]**

K_2SO_4 dissociates completely as follows :

$$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$$

i.e. ions produced = 3
$\therefore$ i = 3
As we know,

$$\therefore\ \pi = iCRT = i\frac{n}{V}RT = i \times \frac{w}{M} \times \frac{1}{V}RT$$

$$\therefore\ \pi = 3 \times \frac{0.025\text{g}}{174\text{g mol}^{-1}} \times \frac{1}{2\text{L}} \times 0.0821 \text{ L atm } K^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$= 5.27 \times 10^{-3}$ atm **[2]**

31. (i) **Cell reaction for Daniell cell**

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

Nernst equation for the above reaction is

$$E_{cell} = E°_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

E_{cell} = decreases when concentration of Zn^{2+} ions increases. **[1]**
This is ,n accordance with Kohlrausch's law

(ii) The molar conductance of water at infinite dilution can be obtained from values of molar conductances at infinite dilution of sodium hydroxide, hydrochloric acid and sodium chloride (all strong electrolytes). This is in accordance with Kohlrausch's law.

$$\Lambda^{\circ}_{m(H_2O)} = \Lambda^{\circ}_{m(NaOH)} + \Lambda^{\circ}_{m(HCl)} - \Lambda^{\circ}_{m(NaCl)}$$ **[1]**

(iii) By the use of direct current, the electrolysis of electrolytic solution takes place. As a result, concentration of electrolyte near the electrodes change which ultimately changes the resistance of the solution. **[1]**

32. The catalytic reaction which depends upon pore-structure of catalyst and the size of the reactant and product molecules is known as shape selective catalysis. Zeolites are good shape-selective catalyst because of their honey comb, like structure. **[1]**

(i) They, are microporous aluminosilicates with Al–O–Si framework and general formula $M_{x/n}\ [(AlO_2)_x\ (SiO_2)]_y\ mH_2O$.

(ii) The reactions taking place in zeolites depend upon the size and shape of the reactant and product molecules as well as upon the pores and cavities of the zeolites.

(iii) Zeolites are widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. They are also used for removing permanent hardness of water.

(iv) e.g. ZSM-5 is a catalyst used in petroleum industry.

$$\text{Alcohols} \xrightarrow[\text{Dehydration}]{\text{ZSM}-5} \text{Gasoline(petrol)}$$

(Amixture of hydrocarbons)

33. (a)

(i) **[1]**

	Experiment	**Ethanal**	**Propanone**
1.	**Tollens Test :** Warm the organic compound with freshly prepared ammonical silver nitrate solution (Tollen's reagent).	A bright silver mirror is produced	No silver mirror is formed
2.	**Fehling Test:** Heat the organic compound with Fehling's reagent.	A reddish bown precipitate is obtained.	No precipitate is obtained
	Any one test		

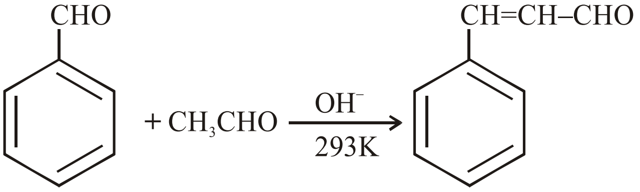
(ii) **[1]**

	Experiment	**Pentan-2-one**	**Pentan-3-one**
	Iodoform Test: The organic compound is heated with iodine in presence of sodium hydroxide solution	A yellow precipitate is obtained	No yellow precipitate is obtained

(b) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4-Dinitrobenzoic acid **[1]**

OR

The carbon atom of the carbonyl group of benzaldehyde is less electrophilic thatn carbon atom of the carbonyl group present in ethanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance hence less reactive than ethanal.



34. (a) Broad spectrum antibiotics :

Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria.

e.g. Chloramphenicol. **[1½]**

(b) Analgesics : Reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system.

e.g. Aspirin/ paracetamol etc. **[1½]**

35. (a) $Fe + 2H^+ \rightarrow H_2 + Fe^{2+}$

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log\frac{[Fe^{2+}]}{[H^+]^2}$$ **[1]**

$$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Fe^{2+}/Fe}$$

$= -0(-0.44) = 0.44$ V **[1]**

$$0.1745 = 0.44 - \frac{0.0591}{2}\log\frac{[0.1]}{[x]^2}$$

Log x = –5

Log[H⁺] = –5

$[H^+] = 10^{-5}$ **[1]**

(b) The mass of copper and silver deposited at the cathode will be different. The amount of different substances deposited by the same quantity of electricity passing through the electrolytic solution are directly proportional to their chemical equivalents. **[2]**

OR

(a) $\Lambda^\circ(CH_3COOH) = \lambda^\circ_{H^+} + \lambda^\circ_{CH_3COO^-}$

$= 349.6 + 40.9 = 390.5$ S cm² mol⁻¹ **[1]**

$$\Lambda_m = \frac{\kappa \times 1000}{c}$$

$$\Lambda_m = \frac{8.0\times10^{-5}\,S\,cm^{-1}\times1000cm^3L^{-1}}{0.0024\,mol\,L^{-1}} = 33.33 S\,cm^2\,mol^{-1}$$ **[1]**

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$$

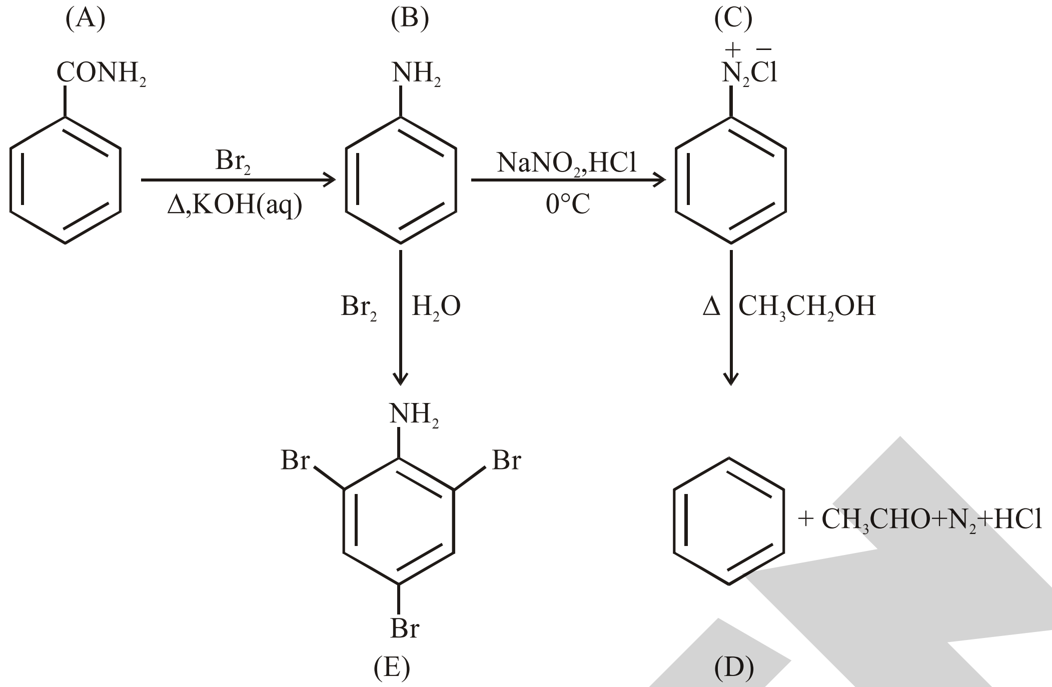
$$\alpha = \frac{33.33\ S\ cm^2\ mol^{-1}}{390.5\ S\ cm^2 mol^{-1}} = 0.085$$ **[1]**

(b) Electrolyte B is a strong electrolyte.

Limiting moalr conductivity increases only to a smaller extent for a strong electrolyte, as on dilution the interionic interactions are overcome.

Limiting molar conductivity increases to a larger extent for a weak electrolyte, as on dilution the degree of dissociation increases, therefore the number of ions in total volume of solution increases. **[2]**

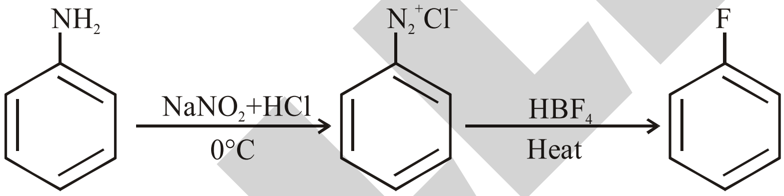
36.



(1/2 × 5 marks for structure and 1/2 ×5 for writing equations)

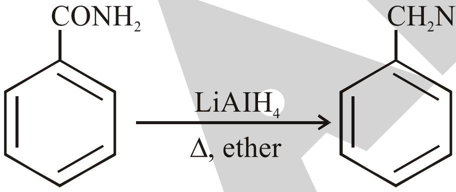
OR

(a) (i)



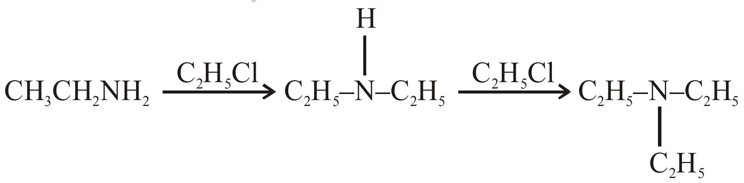
[1]

(ii)



[1]

(iii)



$$CH_3CH_2NH_2 \xrightarrow{C_2H_5Cl} C_2H_5-\overset{H}{\overset{|}{N}}-C_2H_5 \xrightarrow{C_2H_5Cl} C_2H_5-\underset{C_2H_5}{\underset{|}{N}}-C_2H_5$$

[1]

(b) (i) A : $CH_3CH_2CONH_2$

B : $CH_3CH_2NH_2$ **[1]**

(ii) A : $CH_3CH_2CH_2NH_2$

B : $CH_3CH_2CH_2OH$ **[1]**

37. (a) A = $FeCr_2O_4$ B = Na_2CrO_4 C = $Na_2Cr_2O_7$ D = $K_2Cr_2O_7$ **[2]**

(b) (i) 5f, 6d and 7s levels in actinoids are of comparable energies. **[1]**

(ii) this is due to poorer shielding by 5f electrons in actinoids as compared to shielding by 4f electrons in lanthanoids. **[1]**

(iii) In actinoids, 5f electrons are more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Since the outer electrons are less firmly held, they are available for bonding in the actinoids. **[1]**

OR

(a) (i) MnO_4^{2-} ions disproportionate in acidic medium to give permanganate ions and Manganese (IV) oxide.

$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$ **[1]**

(ii) Lanthanum sulphide is formed.

$2La + 3S \xrightarrow{heat} La_2S_3$

(Deduct overall 1/2 mark if equation not balanced/ statements not written) **[1]**

(b) (i) Copper has high enthalpy of atomisation and low enthalpy of hydration. Since the high energy to transform Cu(s) to Cu^{2+}(aq) is not balanced by hydration enthalpy, therefore E°(M^{2+}/M) value for copper is positive (+0.34 V). **[1]**

(ii) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having more stable half filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in extra stable d^5 configuration. **[1]**

(iii) This is due to increasing stability of the species of lower oxidation state to which they are reduced. **[1]**