LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours **ASSIGNTMENT PAPER 11**

Part A

1. (C) **2.** (C) **3.** (C) **4.** (B) **5.** (A) **6.** (C) **7.** (B) **8.** (C) **9.** (A) **10.** (C) **11.** (D) **12.** (B) **13.** (A) **14.** (D)
15. (A) **16.** (A) **17.** (D) **18.** (D) **19.** (A) **20.** (A) **21.** (A) **22.** (D) **23.** (A) **24.** (B) **25.** (D) **26.** (D)
27. (C) **28.** (A) **29.** (D) **30.** (C) **31.** (A) **32.** (A) **33.** (A) **34.** (A) **35.** (B) **36.** (B) **37.** (C) **38.** (D)
39. (B) **40.** (C) **41.** (D) **42.** (B) **43.** (D) **44.** (D) **45.** (D) **46.** (B) **47.** (B) **48.** (C) **49.** (A) **50.** (A)

Part B

Section A

➢ **Write the answer of the following questions : (Each carries 2 Mark)**

1.

➥ We use molten NaCl, the products of electrolysis are sodium metal and Cl_2 gas.

➥ Here, we have only one cation (Na^+) which is reduced at the cathode

Cathode : $Na^+(aq) + e^- \rightarrow Na(s)$ (reduction)

➥ One anion (Cl^-) which is oxidised at the anode

Anode : $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (oxidation)

2.

➥ Reaction → Products

Rate $r_1 = k[A]^2$

(i) When concentration of reactant is doubled;

Rate $r_2 = k[2A]^2 = 4k[A]^2 = 4r_1$

∴ when concentration of the reactant is doubled, the rate of reaction will become 4 times of the initial rate

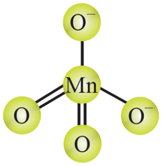
(ii) When concentration of reactant is reduced to half;

Rate $r_2 = k\left[\frac{A}{2}\right]^2 = \frac{1}{4}k[A]^2 = \frac{r_1}{4}$

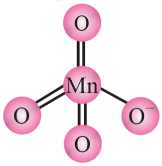
∴ when concentration of the reactant is reduced by half, the rate of reaction will be reduce to $\frac{1}{4}$ of the initial rate.

3.

➥ The manganate and permanganate ions are tetrahedral.



Tetrahedral manganate (green) ion



Tetrahedral permanganate (purple) ion

➥ The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

➥ The π-bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese.

4.

➥ Electronic configuration of Ce : [xe] $4f^1\ 5d^1\ 6s^2$

Ce^{3+} : [xe] $4f^1$ (n = 1)

$\propto = \sqrt{n(n+2)}$ B.M.

$= \sqrt{1(1+2)}$

$= \sqrt{3}$

= 1.73 B.M

5.

➥ When a ligand attaches to the metal ion in a manner that forms a ring, then the metal- ligand association is found to be more stable.

- In other words, we can say that complexes containing chelate rings are more stable than complexes without rings. This is known as the chelate effect.

  e.g. :

  $Ni^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+}$

  $Ni^{2+} + 3en \rightarrow [Ni(en)_3]^{2+}$

  More Stable

6.

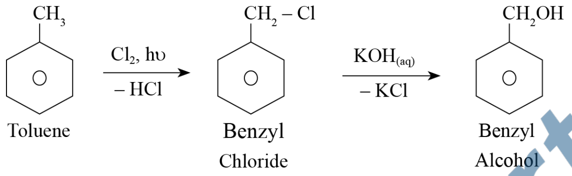
- (5) Homoleptic and Heteroleptic complexes :
  - *"Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic."*

    e.g. : $[Co(NH_3)_6]^{3+}$
  - *"Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic."*

    e.g. : $[Co(NH_3)_4 Cl_2]^{+}$

7.

- Toluene to benzyl alcohol :



8.

- Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide.
- This reaction is known as Wurtz reaction.

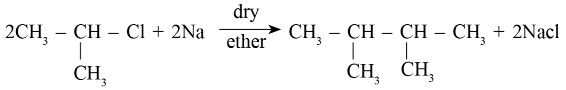
$$2RX + 2Na \xrightarrow[\text{ether}]{\text{dry}} R - R + 2NaX$$

$$2CH_3 - Br + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3 - CH_3 + 2NaBr$$

Bromomethane $\quad$ *n*-Ethane

$$CH_3 - CH_2 - Br + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3 - CH_2 - CH_2 - CH_3 + 2NaBr$$

Bromoethane $\quad$ *n*-butane



$$2CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - Cl + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3 + 2Nacl$$

iso propylchloride $\quad$ 2, 3-dimethylbutune

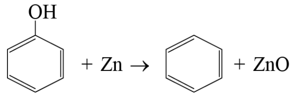
Limitation :

(1) This method is suitable to produce an alkane only with even number of carbon.

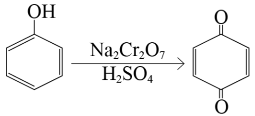
(2) If alkyl halide is tertiary, the alkene is major product.

9.

- Reaction of phenol with zinc dust : Phenol is converted to benzene on heating with zinc dust.



- Oxidation : Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



Benzoquinone

10.

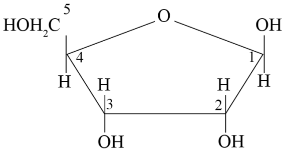
- Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

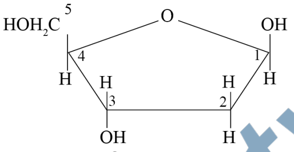
- This reaction is called Stephen reaction.

11.

- Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing hetero cyclic compounds (called bases).
- In DNA molecules the sugar moiety is β-D-2 deoxy-ribose where as in RNA molecule it is β-D-ribose.

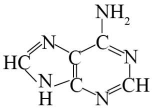


β-D-ribose

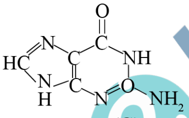


β-D-2-deoxyribose

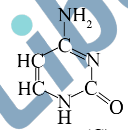
- DNA contains four bases viz, adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



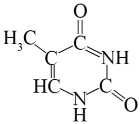
Adenine (A)



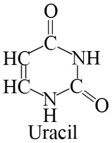
Guanine (G)



Cytosine (C)



Thymine (T)

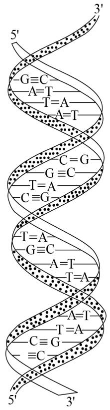


Uracil

(U)

12.

- Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure too.
- James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are wound about each other and held together by hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine where as cytosine forms hydrogen bonds with guanine.



Section B

➢ **Write the answer of the following questions : (Each carries 3 Mark)**

13.

➥

liquid – A	liquid – B
p^{o}_{A} = 450 mm Hg	p^{o}_{B} = 700 mm Hg
$x_A = (?)$	$x_B = (?)$
p_{Total} = 600 mm Hg	
$y_A = (?)$	$y_B = (?)$

➥ According to Raoult's Law

$$p_{Total} = p^{o}_{A} + x_B(p^{o}_{B} - p^{o}_{A})$$

$$\therefore 600 = 450 + x_B(700 - 450)$$

$$\therefore 600 = 450 + 250\, x_B$$

$$\therefore 600 - 450 = 250\, x_B$$

$$\therefore \frac{150}{250} = x_B$$

$$\therefore x_B = 0.6$$

$$x_A + x_B = 1$$

$$\therefore x_A = 1 - x_B$$

$$= 1 - 0.6$$

$$\therefore x_A = 0.4$$

➥ Composition in Vapour phase,

➥

$$p_A = y_A \cdot p_{Total}$$

$$\therefore \frac{p^{o}_{A} \cdot x_A}{p_{Total}} = y_A$$

$$\therefore y_A = \frac{450 \times 0.40}{600}$$

$$\therefore y_A = 0.3$$

$$y_A + y_B = 1$$

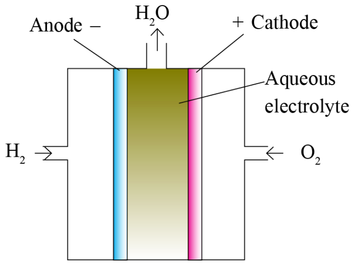
$$\therefore y_B = 1 - y_A$$

$$= 1 - 0.3$$

$$\therefore y_B = 0.7$$

14.

➥ One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water



➥ In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution.

➥ Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions.

➥ The electrode reactions are given below :

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Net reactions : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

15.

- (i) Write differential rate equation:

  Rate = k $[A][B]^2$

- (ii) How is the rate affected on increasing the concentration of B three times ?

  Initial rate $r_1 = k[A][B]^2$

  When concentration of B is increased to three times,

  Rate $r_2 = k[A][3B]^2 = 9k[A][B]^2 = 9r_1$

  ∴ rate becomes nine times.

- (iii) How is the rate affected when the concentration of both A and B are doubled?

  Initial rate $r_1 = k[A][B]^2$

  When concentration of both A and B is increased to two times,

  Rate $r_2 = k[2A][2B]^2 = 8k[A][B]^2 = 8r_1$

  ∴ rate becomes eight times.

16.

- Dichromates are generally prepared from chromate. which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air.
- The reaction with sodium carbonate occurs as follows

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

- The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.\ 2H_2O$ can be crystallised.

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

- Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

  $Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$

- Orange crystals of potassium dichromate crystallise out.
- The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

  $2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

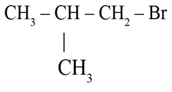
  $Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2\,CrO_4^{2-} + H_2O$

17.

- There are two primary alkyl halides having the formula, C_4H_9Br. They are *n* - bulyl bromide and isobutyl bromide.

$CH_3-CH_2-CH_2-CH_2-Br$

n - Butyl bromide



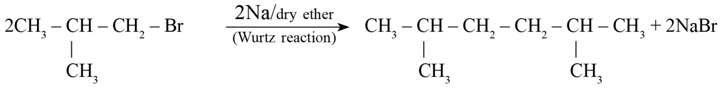
$$\begin{array}{c} CH_3-CH-CH_2-Br \\ | \\ CH_3 \end{array}$$

Isobutyl bromide

- Therefore, compound (a) is either n-butyl bromide or isobutyl bromide.
- Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, C_8H_{18} which is different from the compound formed when n-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

$$2CH_3CH_2CH_2CH_2Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

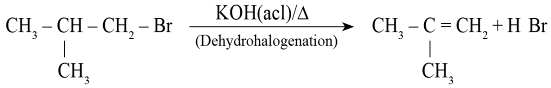
n-Butly bromide — *n*-Octane



$$2CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3+2NaBr$$

Isobutyl bromide (a) 2,5-Dimethylhexane (d)

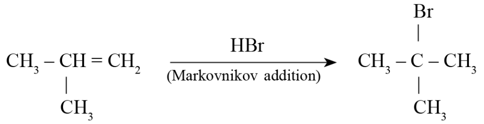
- Thus, compound (d) is 2, 5-dimethylhexane.
- It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2-Methylpropane.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(acl)/}\Delta} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2+H\ Br$$

Isobutyl bromide (a) 2-Methylpropene (b)

- Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a).
- Hence, compound (c) is 2-bromo-2-methylpropane.



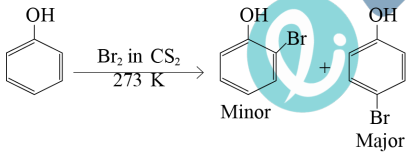
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}=CH_2 \xrightarrow[\text{(Markovnikov addition)}]{\text{HBr}} CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

2-Methylpropene (b) 2-Bromo-2-Methylpropane (c) (as isomer of (a))

18.

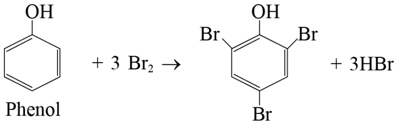
- Halogenation : On treating phenol with bromine, different reaction products are formed under different experimental conditions.

  (a) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.



- The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$, which polarises the halogen molecule. In case of phenol, the polarization of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of –OH group attached to the benzene ring.

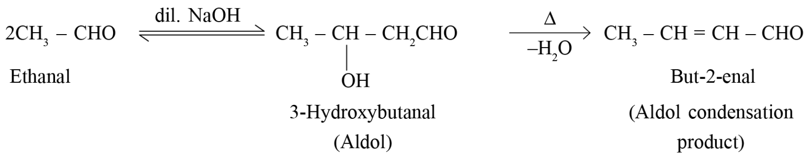
  (b) When phenol is treated with bromine water, 2, 4, 6-tribromophenol is formed as white precipitate.



Phenol 2, 4, 6-Tribromophenol

19.

- Aldol condensation : *"Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively. This is known as Aldol reaction."*

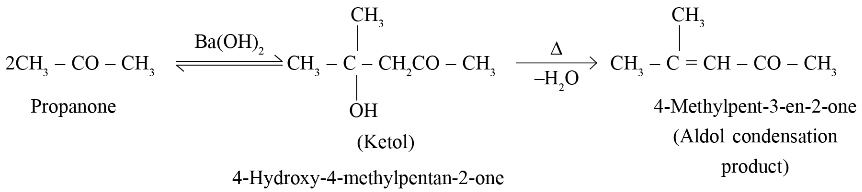


$$2CH_3-CHO \xrightleftharpoons{\text{dil. NaOH}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

Ethanal

3-Hydroxybutanal
(Aldol)

But-2-enal
(Aldol condensation
product)



$$2CH_3-CO-CH_3 \xrightleftharpoons{Ba(OH)_2} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2CO-CH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CO-CH_3$$

Propanone

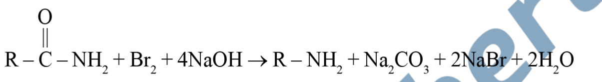
(Ketol)
4-Hydroxy-4-methylpentan-2-one

4-Methylpent-3-en-2-one
(Aldol condensation
product)

- The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give α, β-unsaturated carbonyl compounds which are aldol condensation products and the reaction is called Aldol condensation. Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

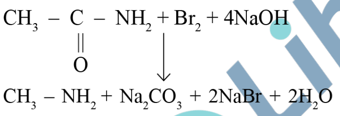
20.

- Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom.
- The amine so formed contains one carbon less than that present in the amide.



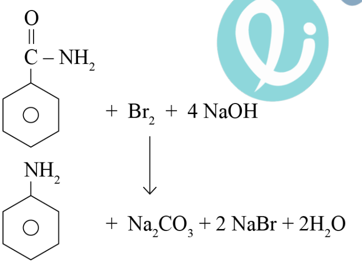
$$R-\overset{\overset{O}{\|}}{C}-NH_2+Br_2+4NaOH \rightarrow R-NH_2+Na_2CO_3+2NaBr+2H_2O$$

Example (1)



$$\begin{array}{c} CH_3-\underset{\underset{O}{\|}}{C}-NH_2+Br_2+4NaOH \\ \downarrow \\ CH_3-NH_2+Na_2CO_3+2NaBr+2H_2O \end{array}$$

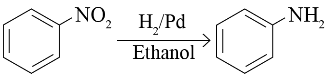
(2)



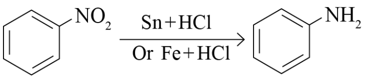
21.

- Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium.
- Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

(i)



(ii)



- Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction.

$Fe + 2HCl \rightarrow H_2 + FeCl_2$

$FeCl_2 + H_2O \rightarrow Fe(OH)_2 + 2HCl$

➥ Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

Section C

➢ **Write the answer of the following questions : (Each carries 4 Mark)**

22.

➥

liquid = A	liquid = B
W_A = 100 g	W_B = 1000 g
M_A = 140 $g.Mol^{-1}$	M_B = 180 $g.Mol^{-1}$
p^o_A = (?)	p^o_B = 500 torr
p_A = (?)	
p_{Total} = 475 torr	

➥ Moles of liquid–A $(n_A) = \frac{W_A}{M_A} = \frac{100}{140} = 0.714$

➥ Moles of liquid–B $(n_B) = \frac{W_B}{M_B} = \frac{1000}{180} = 5.55$

➥ Mole-fraction of liquid–A $(x_A) = \frac{0.714}{0.714 + 5.55}$

$= 0.114$

➥ Mole-fraction of liquid–B $(x_B) = 1 - 0.114$

$= 0.886$

$p_{Total} = p^o_A \,.\, x_A + p^o_B \,.\, x_B$

$475 = p^o_A \,.\, (0.114) + (500)(0.886)$

$\therefore\ 475 = p^o_A \,.\, (0.114) + 443$

$\therefore\ 475 - 443 = p^o_A \,.\, (0.114)$

$\therefore\ 32 = p^o_A \,.\, (0.114)$

$\therefore\ p^o_A = 280.7$ torr

➥ Vapour pressure of pure liquid A is 280.7 torr

➥ Vapour pressure of liq–A in solution

$p_A = p^o_A \,.\, x_A$

$= (280.7) \,.\, (0.114)$

$p_A = 32$ torr

23.

➥ $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

➥ (a) Dry cell

Anode : $Zn(s) \rightarrow Zn^{+2} + 2e^-$

Cathode : $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

➥ (b) Lead storage battery

Anode : $Pb_{(s)} + SO^{-2}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

Cathode : $PbO_{2(s)} + SO^{-2}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow 2PbSO4_{(s)} + 2H_2O$

24.

- Decomposition reaction of azoisopropane,

$$(CH_3)_2CHN = NCH(CH_3)_2 \rightarrow C_6H_{14}(g) + N_2(g)$$

Pressure at time t = 0	35 mm Hg	0	0
Change in pressure	− x	+x	+x
Pressure after t = 360 s	35 − x	+x	+x

$\therefore$ Total pressure after 360 s = 35 – x + x + x = 54 mm Hg

$\therefore$ x = 19

$\therefore$ Pressure after t = 360 s 35 – 19 mm = 16 mm Hg

Calculation of rate constant at 360 s :

- Initial pressure $[R]_0 = p_i = 35$ mm Hg
- Pressure at time t $[R]_t = p_t = 16$ mm Hg
- For first order reaction,

$$k = \frac{2.303}{t} \log \frac{p_i}{p_t}$$

$$= \frac{2.303}{360} \log \frac{35}{16}$$

$$= \frac{2.303}{360} \log 2.1875$$

$$= \frac{2.303}{360} \times 0.3399$$

$$\therefore k = 2.1747 \times 10^{-3} \text{ sec}^{-1}$$

Calculation of k at t = 720 s :

- Total pressure at t = 720 s,
- Total pressure at equilibrium = 35 – x + x + x

= 63 mm Hg

$\therefore$ x = 28

- Initial pressure at time t = 0 s, $[R]_0 = p_i = 35$ mm Hg
- Pressure at time t = 720 s, $[R]_t = p_t = 35 - 28$

= 7 mm Hg

- For first order reaction,

$$k = \frac{2.303}{t} \log \frac{p_i}{p_t}$$

$$= \frac{2.303}{720} \log \frac{35}{7}$$

$$= \frac{2.303}{720} \log 5$$

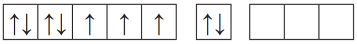
$$= \frac{2.303}{720} \times 0.6990$$

$$\therefore k = 2.21 \times 10^{-3} \text{ sec}^{-1}$$

25.

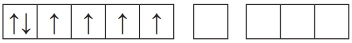
- In $[Co(NH_3)_6]^{3+}$ ion oxidation number of cobalt is +3.
- Electronic configuration of cobalt in ground state.

$_{27}Co$: [Ar] $3d^7$ $4s^2$ 4p



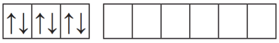
- Electronic configuration of cobalt in +3 oxidation state.

$_{27}Co^{+3}$: [Ar] $3d^6$ 4s 4p



- NH_3 is strong ligand so electrons get paired in d-orbital and d^2sp^3 hybridisation occurs.

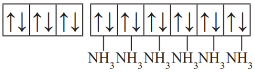
Co^{+3} : [Ar] $3d^6$



Six d^2sp^3 hybrid orbitals

$[Co(NH_3)_6]^{+3}$: $3d^6$

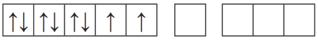
(inner orbital or low spin complex



Six pairs of electrons from six NH_3 molecules

- Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals.
- Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron.
- In the formation of this complex, since the inner d orbital (3d) is used in hybridization, the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complex.
- In $[Ni(NH_3)_6]^{2+}$ ion oxidation state of Ni is +2.
- Electronic configuration of Ni^{2+} ion.

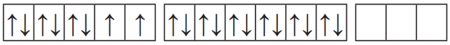
$_{28}Ni^{2+}$: [Ar] 3d 4s 4p



- If NH_3 causes the pairing, then 3d orbital is not empty. Thus, it cannot undergo d^2sp^3 hybridization Therefore, it undergoes sp^3d^2 hybridization.

$[Ni(NH_3)_6]^{2+}$

3d sp^3d^2 4d



Six pair of electrons from six NH_3 molecules

- Hence, it forms an outer orbital complex.

26.

- Propoxypropane from propan-1-ol can be synthesised by two different methods :

1. By Williamson synthesis:

$3\,CH_3-CH_2-CH_2-OH + PBr_3 \rightarrow 3\,CH_3-CH_2-CH_2-Br + H_3PO_3$

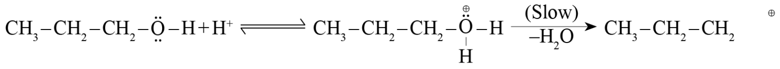
Propan-1-ol 1-Bromopropane

$CH_3-CH_2-CH_2-OH + Na \rightarrow CH_3-CH_2-CH_2-\bar{O}\,\overset{+}{Na} + \frac{1}{2}H_2$

Propan-1-ol Sodium propoxide

$$CH_3-CH_2-CH_2-ONa + CH_3-CH_2-CH_2-Br \xrightarrow{(S_N2)} CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3 + NaBr$$

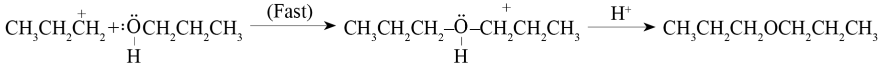
2. By acid-dehydration of alcohol :



$$CH_3-CH_2-CH_2-\ddot{\underset{..}{O}}-H + H^+ \rightleftharpoons CH_3-CH_2-CH_2-\underset{H}{\overset{\oplus}{\ddot{O}}}-H \xrightarrow[-H_2O]{(Slow)} CH_3-CH_2-\overset{\oplus}{C}H_2$$

Propan-1-ol Protonated alcohol 1° Carbocation

- Primary carbocation attacks on another molecule of propan-1-ol via S_N1 mechanism.

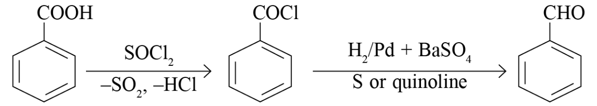


$$CH_3CH_2\overset{+}{C}H_2 + :\underset{H}{\ddot{O}}CH_2CH_2CH_3 \xrightarrow{(Fast)} CH_3CH_2CH_2-\underset{H}{\overset{+}{\ddot{O}}}-CH_2CH_2CH_3 \xrightarrow{H^+} CH_3CH_2CH_2OCH_2CH_2CH_3$$

Protonated ether 1-Propoxypropane

27.

- (ii) Benzoic acid to benzaldehyde :



Benzoic acid Benzaldehyde

(iv) Benzene to *m*-nitroacetophenone :