

LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours

ASSIGNMENT PAPER 10

Part A

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



Part B

Section A

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

1.

➤ $R = 1500 \Omega$, $G^* = (?)$, $k = 0.146 \times 10^{-3} \text{ S cm}^{-1}$
 cell constant (G^*) = $R \cdot K$
 $= (1500) \times (0.146 \times 10^{-3})$
 $= 0.219 \text{ cm}^{-1}$

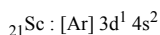
2.

➤ $k = 2.0 \times 10^{-2} \text{ sec}^{-1}$
 $[R]_0 = 1 \text{ mol L}^{-1}$, $t = 100 \text{ sec}$
 $[R]_t = ?$

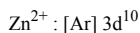
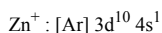
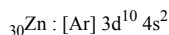
➤ $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$
 $\therefore \log \frac{[R]_0}{[R]_t} = \frac{k \times t}{2.303}$
 $\therefore \log \frac{[R]_0}{[R]_t} = \frac{2.0 \times 10^{-2} \times 100}{2.303}$
 $\therefore \log \frac{[R]_0}{[R]_t} = 0.8684$
 $\therefore \frac{[R]_0}{[R]_t} = \text{anti log } 0.8684 = 7.3863$
 $\therefore [R]_t = \frac{[R]_0}{7.3863} = \frac{1}{7.3863} = 0.1354 \text{ mol L}^{-1}$

3.

➤ On the basis of incompletely filled 3d orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element.



➤ On the other hand, zinc atom has completely filled d orbitals ($3d^{10}$) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.



4.

➤ Electronic configuration of Mn^{2+} is $[\text{Ar}]^{18}3d^5$.

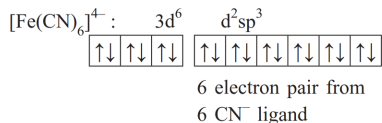
➤ Electronic configuration of Fe^{2+} is $[\text{Ar}]^{18}3d^6$.

➤ It is known that half-filled and fully-filled orbitals are more stable. Therefore, Mn in (+2) state has a stable d^5 configuration. This is the reason Mn^{2+} shows resistance to oxidation to Mn^{3+} . Also, Fe^{2+} has $3d^6$ configuration and by losing one electron, its configuration changes to a more stable $3d^5$ configuration. Therefore, Fe^{2+} easily gets oxidized to Fe^{+3} oxidation state.

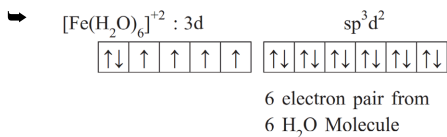
5.

➔ The colour of a particular coordination compound depends on the magnitude of the crystal-field splitting energy, Δ_o . This CFSE in turn depends on the nature of the ligand. In case of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, the colour differs because there is a difference in the CFSE. Now, CN^- is a strong field ligand having a higher CFSE value as compared to the CFSE value of water. This means that the absorption of energy for the intra d-d transition also differs. Hence, the transmitted colour also differs.

➔ In $[\text{Fe}(\text{CN})_6]^{4-}$ complex ion CN^- ligand is strong ligand so no unpaired electron in 3d orbital and d-d transition does not occur.

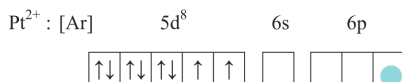


➔ While in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ complex ion H_2O is weak ligand so there are 4 unpaired electron so, both complex show different colours in its dilute solution.

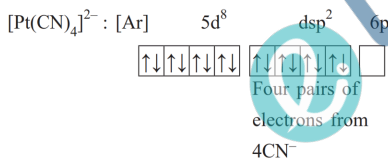


6.

➔ In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes dsp^2 hybridization. Now, the electronic configuration of Pt^{2+} is $[\text{Ar}] 5d^8 6s^0$



➔ CN^- being a strong field ligand causes the pairing of unpaired electrons. Hence, there are no unpaired electrons in $[\text{Pt}(\text{CN})_4]^{2-}$

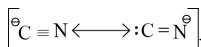


7.

➔ Ambident nucleophiles are nucleophiles having two nucleophilic sites. Thus, ambident nucleophiles have two sites through which they can attack.

➔ Groups like cyanides and nitrites possess two nucleophilic centres are called ambident nucleophiles.

➔ Cyanide group is a hybrid of two contributing structures and therefore, it can act as a nucleophile in two different ways



➔ The Linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides.

➔ Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage $[\text{O} - \ddot{\text{N}} = \text{O}]$.

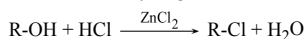
➔ The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

8.

➔ 2° - carbocation is more stable than 1° - carbocation so $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ easily hydrolysed.

9.

➤ Alcohols react with hydrogen halides to form alkyl halides.



➤ The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another.

➤ Alcohols are soluble in Lucas reagent (conc. HCl and ZnCl_2) while their halides are immiscible and produce turbidity in solution.

➤ In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily.

➤ Primary alcohols do not produce turbidity at room temperature.

➤ This is how alcohols can be distinguished by Lucas test.

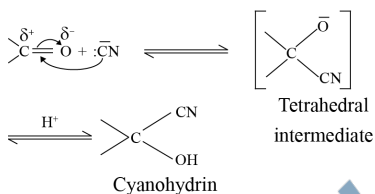
10.

➤ Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins.

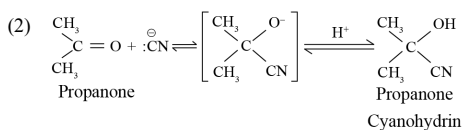
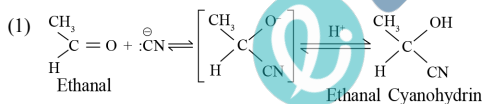
➤ This reaction occurs very slowly with pure HCN.

➤ Therefore, it is catalysed by a base and generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

➤ Cyanohydrins are useful synthetic intermediates.



e.g :



11.

➤ Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following 3 groups

➤ (i) Monosaccharide compounds :

➤ "A carbohydrate that can not be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide.

➤ About 20 monosaccharides are known to occur in nature. Some common examples are glucose, fructose, ribose, etc.

➔ (ii) Oligosaccharide compounds :

- "Carbohydrates that yield two to ten monosaccharide units, on hydrolysis are called oligosaccharides."
- They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides they provide on hydrolysis.
- Amongst these the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different.
- For example, one molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose where as maltose gives two molecules of only glucose.

➔ (iii) Polysaccharide compounds :

- "Carbohydrate which yield a large number of monosaccharide units on hydrolysis are called polysaccharides."
- Some common examples are starch, cellulose, glycogen, gums etc. Polysaccharides are not sweet in taste. Hence, they are also called non-sugars.

12.

- ➔ Carbohydrate compounds are classified as reducing sugars and non reducing sugars.
- ➔ Reducing sugars are carbohydrates that reduce Fehling's solution and Tollen's reagent. All monosaccharides and disaccharides, excluding sucrose, are reducing sugars.

Section B

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

13.

➔ $W_2 = 25 \text{ g}$ $W_1 = 450 \text{ g}$
 $M_2 = 180 \text{ g.Mol}^{-1}$ $M_1 = 18 \text{ g.Mol}^{-1}$
 $p_1^0 = 17.535$ $p_1 = (?)$

$$n_1 = \frac{W_1}{M_1} = \frac{450}{18} = 25$$
$$n_2 = \frac{W_2}{M_2} = \frac{25}{180} = 0.14$$
$$\therefore \frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$
$$\therefore \frac{17.535 - p_1}{17.535} = \frac{0.14}{25.14}$$
$$\therefore 17.535 - p_1 = \frac{0.14 \times 17.535}{25.14}$$
$$\therefore 17.535 - p_1 = 0.0976$$
$$\therefore p_1 = 17.535 - 0.0976$$
$$= 17.44 \text{ mm Hg}$$

14.

➔ $\lambda_m^0(\text{HCOOH}) = \lambda_m^0 \text{H}^+ + \lambda_m^0(\text{HCOO}^-)$
 $= 349.6 + 54.6$
 $= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$

➔ degree of dissociation (α) = $\frac{\Lambda_m}{\Lambda_m^0}$
 $= \frac{46.1}{404.2}$
 $= 0.1140$

$$\begin{aligned} \rightarrow \text{dissociation } (k_a) &= \frac{\alpha^2 \cdot c}{1 - \alpha} \\ &= \frac{(0.1140)^2 \times 0.025}{1 - 0.1140} \\ &= \frac{3.249 \times 10^{-4}}{0.886} \end{aligned}$$

$$\rightarrow k_a = 3.67 \times 10^{-4} \text{ mol L}^{-1}$$

15.

→ Suppose,

Order of reaction with respect to A = x

Order of reaction with respect to B = y

→ Then,

$$\text{Rate} = k [A]^x [B]^y$$

$$\rightarrow \therefore r_1 = k[0.20]^x [0.30]^y = 5.07 \times 10^{-5} \dots \dots (1)$$

$$r_2 = k[0.20]^x [0.10]^y = 5.07 \times 10^{-5} \dots \dots (2)$$

$$r_3 = k[0.40]^x [0.05]^y = 1.43 \times 10^{-4} \dots \dots (3)$$

Dividing (1) and (2) we get,

$$\frac{r_1}{r_2} = \frac{k[0.20]^x [0.30]^y}{k[0.20]^x [0.10]^y} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = 1$$

$$\therefore \frac{r_1}{r_2} = [3]^y = 1$$

$$\therefore y = 0, \text{ because } [3]^0 = 1 = [3]^y$$

Dividing (3) and (2) we get,

$$\rightarrow \frac{r_3}{r_2} = \frac{k[0.40]^x [0.05]^y}{k[0.20]^x [0.10]^y} = \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = 2.82$$

$$\rightarrow \therefore \frac{r_3}{r_2} = \frac{k[0.40]^x [0.05]^0}{k[0.20]^x [0.10]^0} = 2.82$$

$$\rightarrow \therefore [2]^x = 2.82$$

Taking log of both the side we get,

$$\log [2]^x = \log 2.82$$

$$\therefore x \log 2 = \log 2.82$$

$$x \times 0.3010 = 0.4503$$

$$\therefore x = \frac{0.4503}{0.3010} = 1.5$$

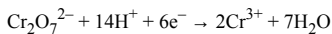
\therefore order of reaction with respect to A = 1.5

order of reaction with respect to B = 0

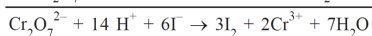
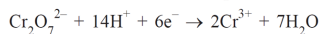
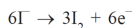
16.

→ Potassium dichromates are strong oxidising agents

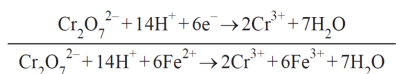
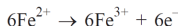
→ In acidic solution, its oxidising action can be represented as follows



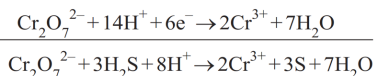
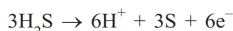
(i) Acidified potassium dichromate will oxidise iodides to iodine,



(ii) Acidified potassium dichromate will oxidise iron (ii) solution to iron (iii) solution

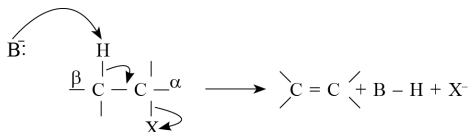


(iii) Acidified potassium dichromate will oxidise H₂S to sulphur.



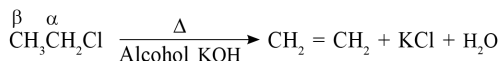
17.

➤ When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from βcarbon and a halogen atom from the α-carbon atom.



B = Base ; X=Leaving group

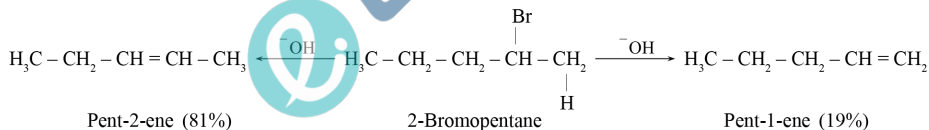
➤ As a result, an alkene is formed as a product. Since β-hydrogen atom is involved in elimination, it is often called β-elimination.



➤ If there is possibility of formation of more than one alkene due to the availability of more than one β-hydrogen atoms, usually one alkene is formed as the major product.

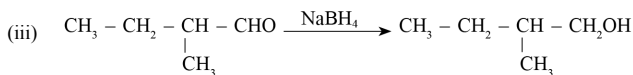
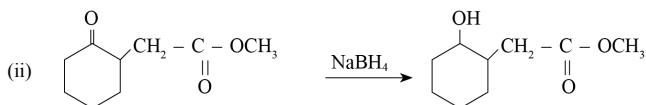
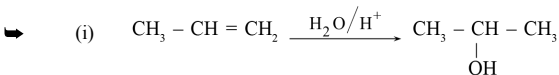
➤ These form part of a pattern was first observed by Russian chemist, Alexander Zaitsev (also pronounced as Saytzeff).

➤ A rule which can be summarised as “in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.”



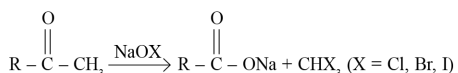
➤ Thus, 2-bromopentane gives pent-2-ene as the major product.

18.

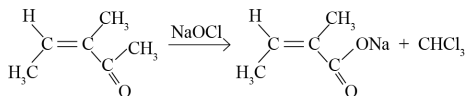


19.

- Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salt of corresponding carboxylic acid having one carbon atom less than that of carbonyl compound.



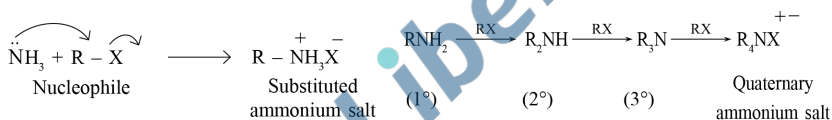
- The methyl group is converted to haloform.
- This oxidation does not affect a carbon-carbon double bond, if present in the molecule.



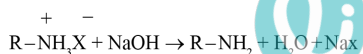
- Iodoform reaction with sodium hypoiodite is also used for detection of CH_3CO group or $\text{CH}_3\text{CH}(\text{OH})$ group which produces CH_3CO group on oxidation.

20.

- The carbon-halogen bond in alkyl or benzyl halides can be easily cleaved by nucleophile.
- Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-\text{NH}_2$) group.
- This process of cleavage of the $\text{C}-\text{X}$ bond by ammonia molecule is known as ammonolysis.
- The reaction is carried out in a sealed tube at 373 K.
- The primary amine obtained which behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.



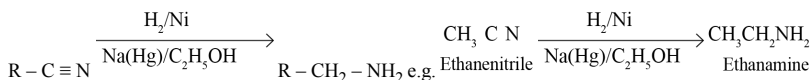
- The free amine can be obtained from the ammonium salt by treatment with a strong base:



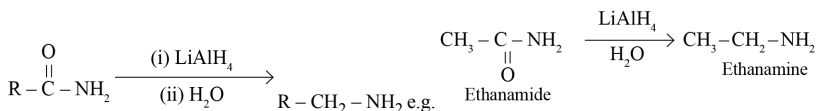
- Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.
- However, primary amine is obtained as a major product by taking large excess of ammonia.
- The order of reactivity of halides with amines is $\text{RI} > \text{RBr} > \text{RCl}$.

21.

- Nitriles on reduction with lithium aluminium hydride (LiAlH_4) or catalytic hydrogenation produce primary amines. This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.



- The amides on reduction with lithium aluminium hydride yield amines.



Section C

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

22.

➤ "The solutions which does not follows Raoult's law over the entire range of concentration are known as Non ideal solutions."

➤ The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law

➤ If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult's law.

➤ For Non-ideal solution $\Delta_{\text{mix}} H \neq 0$ and $\Delta_{\text{mix}} V \neq 0$

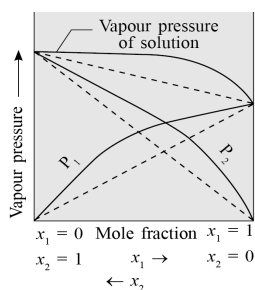
(1) Positive deviation :

➤ "In positive deviation vapour pressure of solution is higher than that of Raoult's law."

➤ In positive deviation $\Delta_{\text{mix}} H > 0$, $\Delta_{\text{mix}} V > 0$

➤ In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B.

➤ In this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules.



➤ This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour pressure and result in positive deviation.

➤ Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

➤ In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.

(2) Negative deviation :

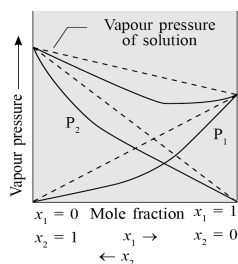
➤ "In negative deviation the vapour pressure of solution is lower than that of Raoult's Law."

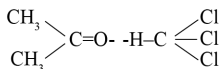
➤ In negative deviation $\Delta_{\text{mix}} H < 0$, $\Delta_{\text{mix}} V < 0$

➤ In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviations.

➤ Mixture of phenol and aniline is show negative deviation. the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules.

➤ Mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.

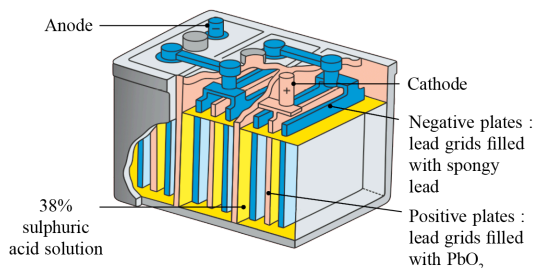




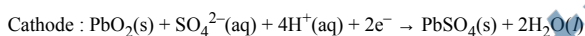
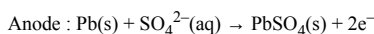
- ➔ This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law

23.

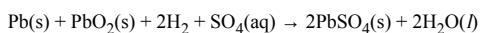
- ➔ It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode.
- ➔ A 38% solution of sulphuric acid is used as an electrolyte.



- ➔ The cell reactions when the battery is in use are given below :



- ➔ Overall cell reaction consisting of cathode and anode reactions is :



- ➔ On charging the battery, the reaction is reversed and $\text{PbSO}_4(\text{s})$ on the anode and cathode is converted into Pb and PbO_2 , respectively.

24.

- ➔ Collision theory, which was developed by Max Trautz and William Lewis in 1916-18, provides greater insight into the energetic and mechanistic aspects of reaction.

- ➔ It is based on kinetic theory of gases.

- ➔ According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

- ➔ "The number of collision per second per unit volume of the reaction mixture is known as collision frequency (Z)."

- ➔ Another factor which affects the rate of chemical reaction is activation energy.

- ➔ For a bimolecular elementary reaction

- ➔ $\text{A} + \text{B} \rightarrow \text{Products}$

- ➔ Rate of reaction can be expressed as

$$\text{Rate} = Z_{\text{AB}} e^{-\frac{E_a}{RT}} \dots \dots \text{Eq. (1)}$$

- ➔ where Z_{AB} represents the collision frequency of reactants A and B, and $e^{-\frac{E_a}{RT}}$ represents the fraction of molecules with energies equal to or greater than E_a .

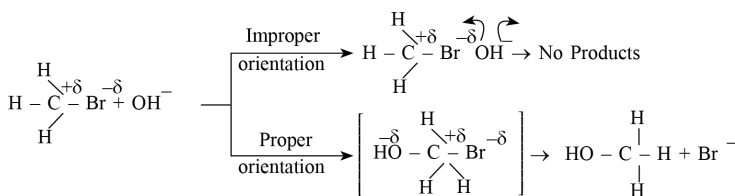
- ➔ Comparing equation (1) with Arrhenius equation, we can say that A is related to collision frequency.

- ➔ Equation (1) predicts the value of rate constant fairly accurately for the reaction that involve atomic species or simple molecule but for complex molecules significant deviations are observed.

- ➔ The reason could be that all collision do not lead to the formation of products.

- ➔ "The collision in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collision."

- For example, formation of methanol from bromomethane $\text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$ depends upon the orientation of reactant molecule as shown in figure.



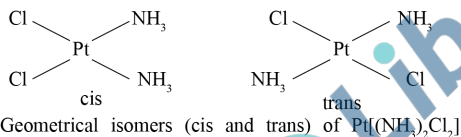
- Intermediate
- The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no product are formed.
- To account for effective collision, another factor P, called the probability factor or steric factor is introduced.
- It takes into account the fact that in a collision, molecules be properly oriented i.e.

$$\text{Rate} = PZ_{AB} e^{-\frac{E_a}{RT}}$$

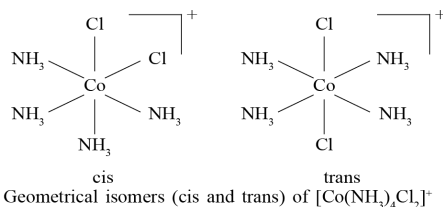
- Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of chemical reaction.

25.

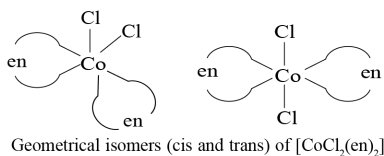
- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.
- Important examples of these behaviour are found with coordination numbers 4 and 6.
- In a square planar complex of formula $[\text{MX}_2\text{L}_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer.



- Other square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers-two cis and one trans.
- Such isomerism is not possible for a tetrahedral geometry.
- In octahedral complexes of formula $[\text{MX}_2\text{L}_4]$ in which the two ligands X may be oriented cis or trans to each other



- This type of isomerism also arises when didentate ligands L-L [e.g., en] are present in complexes of formula $[\text{MX}_2(\text{L-L})_2]$



- Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$.
- If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, it forms the facial (fac) isomer.

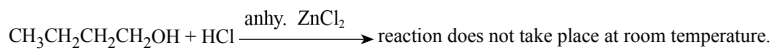
➔ When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.



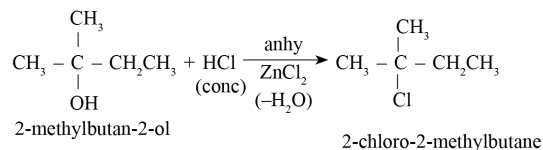
The facial (fac) and meridional (mer) isomers of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$

26.

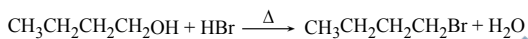
➔ (a) With HCl-ZnCl_2 :



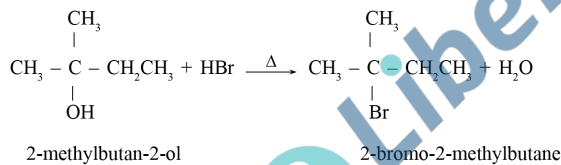
Butan-1-ol



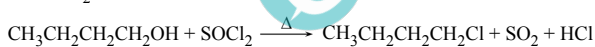
➔ (b) With HBr :



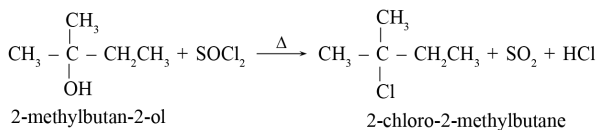
Butan-1-ol 1-bromobutane



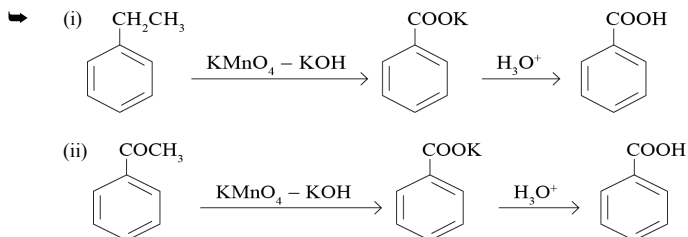
➔ (c) With SOCl_2 :

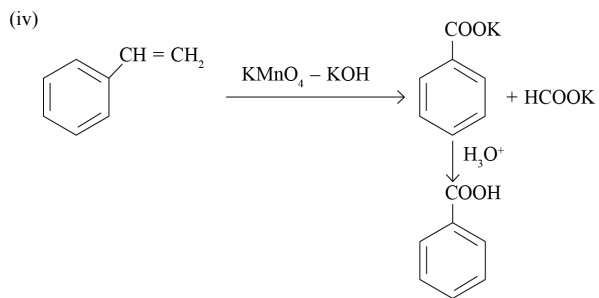
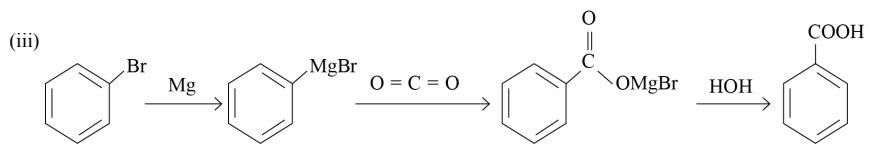


Butan-1-ol 1-bromobutane



27.





 Liberty