

LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours

ASSIGNMENT PAPER 9

Part A

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



Part B

Section A

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

1.

➤ $I = 5A$

$t = 8 \text{ min } 45 \text{ sec}$

$= (8 \times 60) + 45$

$= 480 + 45$

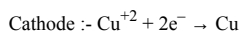
$t = 525 \text{ sec}$

$Q = It$

$= 5 \times 525$

$= 2625 \text{ C}$

$\therefore F = \frac{2625}{96500}$



2F gives 1 mol Cu

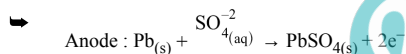
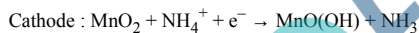
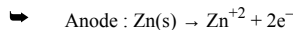
$\therefore \frac{2625}{96500}$ gives (?)

$\text{mol} = \frac{2625 \times 1}{96500 \times 2}$

$\frac{\text{mass}}{63.5} = 0.0136$

$\text{mass} = 0.8636 \text{ gm}$

2.



3.

➤ The order of a reaction is sometimes altered by conditions.

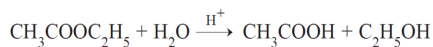
➤ There are many reactions which obey first order rate law although they are higher order reactions.

➤ Consider the hydrolysis of ethyl acetate which is a chemical reaction between ethyl acetate and water. In reality, it is second order reaction and concentration of both ethyl acetate and water affect the rate of the reaction.

➤ But water is taken in large excess for hydrolysis, therefore, concentration of water is not altered much during the reaction.

➤ Thus, the rate of reaction is affected by concentration of ethyl acetate.

➤ For e.g. 0.01 mol ethyl acetate react with 10 mol of water amounts of the reactants and products at the beginning ($t = 0$) and completion (t) of the reaction are give as under.

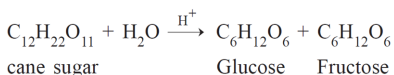


$t = 0$ 0.01 mol 10 mol 0 mol 0 mol

$t = t$ 0 mol 9.99 mol 0.01 mol 0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Inversion of cane sugar is another pseudo first order reaction.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

4.

- ➔ Suppose initial concentration $[\text{R}]_0 = 100$
- ➔ \therefore Concentration at time t $[\text{R}]_t = 70$, (30% decomposition).
- ➔ $t = 40$ min.

➔ Comparing $k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]_t}$ and

$$k = \frac{0.693}{\frac{t_1}{2}} \text{ we get,}$$

$$\frac{0.693}{\frac{t_1}{2}} = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]_t}$$

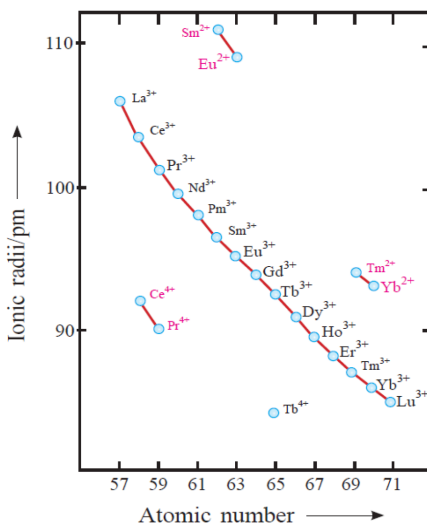
$$\therefore \frac{0.693}{\frac{t_1}{2}} = \frac{2.303}{40} \log \frac{100}{70} = \frac{2.303}{40} \times 0.1549$$

$$\therefore \frac{0.693}{\frac{t_1}{2}} = 0.0089185$$

$$\therefore \frac{t_1}{2} = 0.693 / 0.0089185 = 77.7 \text{ min}$$

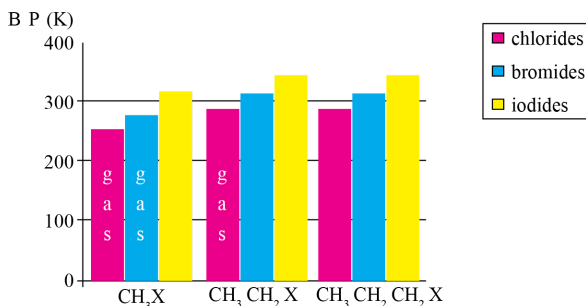
5.

- ➔ As we move along the lanthanoid series, the atomic number increases gradually by one. This means that the number of electrons and protons present in an atom also increases by one.
- ➔ As electrons are being added to the same shell, the effective nuclear charge increases.
- ➔ This happens because the increase in nuclear attraction due to the addition of proton is more pronounced than the increase in the interelectronic repulsions due to the addition of electron.
- ➔ Also, with the increase in atomic number, the number of electrons in the 4f orbital also increases. The 4f electrons have poor shielding effect.
- ➔ Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the attraction of the nucleus for the outermost electrons increases.
- ➔ This results in a steady decrease in the size of lanthanoids with the increase in the atomic number. This is termed as lanthanoid contraction.



➤ That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

➤ The pattern of variation of boiling points of different halides is depicted in Fig.



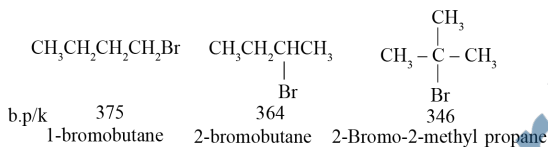
Comparison of boiling points of some alkyl halides

➤ For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI > RBr > RCl > RF.

➤ This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

➤ The boiling points of isomeric haloalkanes decrease with increase in branching ($1^0 > 2^0 > 3^0$).

➤ For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.



11.

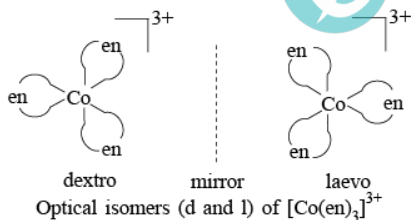
➤ Optical isomers are mirror images that cannot be superimposed on one another.

➤ These are called as enantiomers.

➤ The molecules or ions that cannot be superimposed are called chiral.

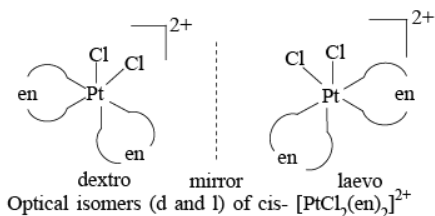
➤ The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter.

➤ Dextro (d) rotates plane polarised light to the right, and laevo (l) rotates plane polarised light to the left.



➤ Optical isomerism is common in octahedral complexes involving didentate ligands

➤ In a coordination entity of the type $[\text{PtCl}_2(\text{en})_2]^{2+}$, only the cis isomer shows optical activity.



12.

- ➔ Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3, 5-dinitrophenol, 2, 4, 6-trinitrophenol.

Section B

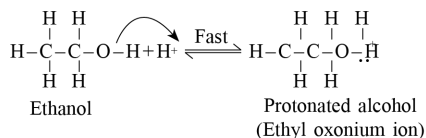
➤ Write the answer of the following questions : (Each carries 3 Mark)

13.

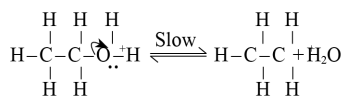
- ➔ The mechanism of dehydration of ethanol involves the following steps :

➔ Mechanism :

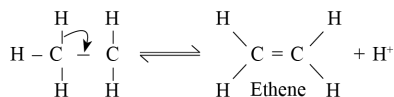
➔ Step 1 : Formation of protonated alcohol



➔ Step 2 : Formation of carbocation : It is the slowest step and hence, the rate determining step of the reaction.



➔ Step 3 : Formation of ethene by elimination of a proton.



➔ The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

14.

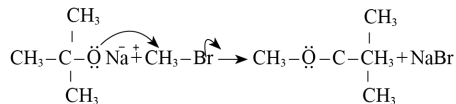
➔ Williamson synthesis is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers.

➔ However, selection of appropriate reactants is required for the preparation of unsymmetrical ethers.

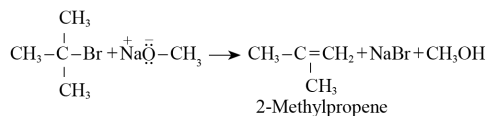
➔ Williamson synthesis occurs via S_N2 mechanism and primary alkyl halides are more reactive towards S_N2 reaction.

➔ Thus, better results are obtained if the alkyl halide is primary and alkoxide ion is primary, secondary or tertiary.

➔ For example, tert-butyl ether can be prepared by treating methyl bromide with tert-butoxide ion.



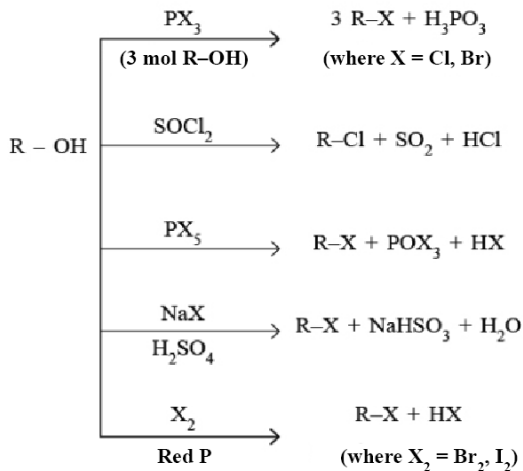
➔ The above ether can not be prepared by the reaction between sodium methoxide and tert-butyl bromide. Because in this case elimination competes over substitution and alkene compound iso-butylene obtain as a product.



➔ It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

➔ Aryl and vinyl halides can not be used as reactant in Williamson synthesis as they are very less reactive towards nucleophilic reaction.

15.



16.

➤ Suppose,

Order of reaction with respect to A = x

Order of reaction with respect to B = y

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

$$\therefore r_1 = k[0.1]^x[0.1]^y = 6.0 \times 10^{-3} \dots \dots (1)$$

$$r_2 = k[0.3]^x[0.2]^y = 7.2 \times 10^{-2} \dots \dots (2)$$

$$r_3 = k[0.3]^x[0.4]^y = 2.88 \times 10^{-1} \dots \dots (3)$$

$$r_4 = k[0.4]^x[0.1]^y = 2.40 \times 10^{-2} \dots \dots (4)$$

Dividing (4) and (1) we get,

$$\frac{r_4}{r_1} = \frac{k[0.4]^x[0.1]^y}{k[0.1]^x[0.1]^y} = \frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = 4$$

$$\therefore \frac{r_4}{r_1} = [4]^x = [4]^1$$

$$\therefore x = 1$$

➤ Order of reaction with respect to A = 1

Dividing (3) and (2) we get,

$$\frac{r_3}{r_2} = \frac{k[0.3]^x[0.4]^y}{k[0.3]^x[0.2]^y} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = 4$$

$$\therefore \frac{r_3}{r_2} = [2]^y = 4 = [2]^2$$

$$\therefore y = 2$$

∴ order of reaction with respect to A = 1

➤ order of reaction with respect to B = 2

➤ overall order of reaction = 3

∴ rate equation,

$$\text{Rate} = k[\text{A}]^1[\text{B}]^2$$

➤ Calculation of rate constant k

From equation (1)

$$\begin{aligned} r_1 &= k[0.1]^1[0.1]^2 = 6.0 \times 10^{-3} \\ k &= \frac{6.0 \times 10^{-3}}{[0.1]^1[0.1]^2} = \frac{6.0 \times 10^{-3}}{[10]^{-1}[10]^{-2}} \\ &= 6.0 \text{ mol}^{-2} \text{ L}^{-2} \text{ min}^{-1} \end{aligned}$$

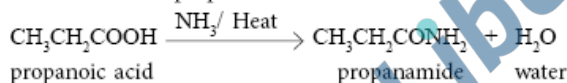
17.

$$\begin{aligned} W_2 &= 45 \text{ g } W_1 = 600 \text{ g} \\ M_2 &= 62 \text{ g.Mol}^{-1} \text{ Kf} = 1.86 \text{ K.kg.Mol}^{-1} \\ \Delta T_f &= (?) \quad T_f = (?) \\ \Delta T_f &= K_f \cdot \frac{W_2 \times 1000}{M_2 \times W_1} \\ &= 1.86 \times \frac{45 \times 1000}{62 \times 600} \\ \Delta T_f &= 2.25 \text{ K} \\ \Delta T_f &= T_f^0 - T_f \\ \therefore 2.25 &= 273.15 - T_f \\ \therefore T_f &= 273.15 - 2.25 \\ T_f &= 270.9 \text{ K} \end{aligned}$$

18.

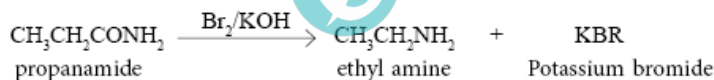
Conversion of propanoic acid to ethanoic acid

Step 1 : Formation of propionamide



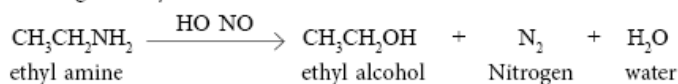
Step 2 : Formation of ethyl amine

Further treatment with bromide and potassium hydroxide (Hoffmann bromide degradation process) results in propionamide ethyl amine.



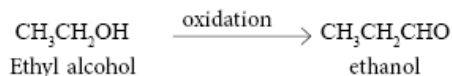
Stage 3 : Formation of ethyl alcohol

Diazotization gives ethyl amine ethanol.



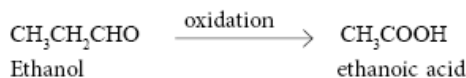
Stage 4 : Formation of Ethanol

Oxidation of ethyl alcohol gives ienal.



Step 5 : Formation of ethanoic acid

Oxidation of enal gives ethanoic acid.



19.

➤ "Ligands are atom or ions which donates electron pairs to the central metal ion."

(OR)

➤ "The ions or molecules bound to the central atom/ion in the coordination entity are called ligands."

➤ These may be simple ions such as Cl^- , small molecules such as H_2O or NH_3 , larger molecules such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or even macromolecules, such as proteins.

➤ Classification of Ligands :

➤ (1) Unidentate ligands :

▮▮▮ "When a ligand is bound to a metal ion through a single donor atom, the ligand is said to be unidentate."

Example :

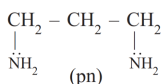
(a) Neutral : $\text{H}_2\ddot{\text{O}}:$, $:\text{NH}_3:$, $:\text{CO}:$, $:\text{NO}:$, $\text{CH}_3\ddot{\text{N}}\text{H}_2$, $\text{C}_5\text{H}_5\ddot{\text{N}}$ (py)

(b) Negative ion : OH^- , F^- , Cl^- , Br^- , I^- , CN^- , NH_2^- , NO_3^- , NO_2^- , NCH_3COO^- (AcO⁻), O^{2-} , S^{2-} , N^{3-}

➤ (2) Didentate ligands :

▮▮▮ "When a ligand is bound to a metal ion through a two donor atom, the ligand is said to be didentate."

(a) Neutral : $\text{H}_2\ddot{\text{N}}^-$, $-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$ (en),



Negative ion : CO_3^{2-} , SO_4^{2-} , COO^-

(b) Negative ion : COO^- (OX)²⁻

➤ (3) Tridentate ligands :

▮▮▮ "When a ligand is bound to a metal ion through a three donor atom, the ligand is said to be Tridentate."

Example :

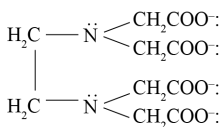
(a) Neutral : $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \text{ (ptn)} \\ | \quad | \quad | \\ \text{:NH}_2 \quad \text{:NH}_2 \quad \text{:NH}_2 \end{array}$

(b) Negative ion : PO_4^{3-} , AsO_4^{3-}

(4) Hexadentate ligands :

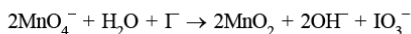
➤ When a ligand is bound to a metal ion through a six donor atom, the ligand is said to be hexadentate

Example : Ethylenediaminetetraacetate ion (EDTA⁴⁻)

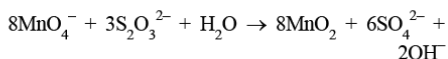


20.

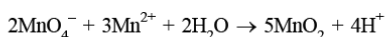
(a) A notable reaction is the oxidation of iodide to iodate:



(b) Thiosulphate is oxidised almost quantitatively to sulphate :



(c) Manganous salt is oxidised to MnO_2 ; the presence of zinc sulphate or zinc oxide catalyses the oxidation :



21.

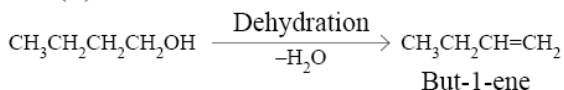
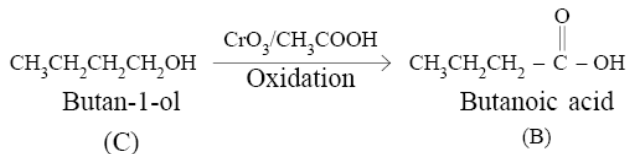
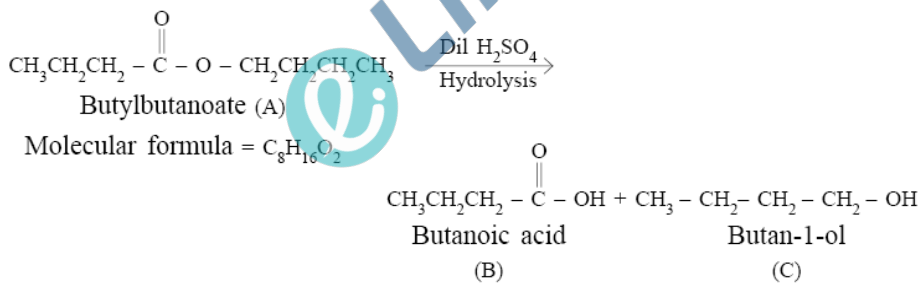
- "The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance"
- When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases.
- The conductivity of electrolytic (ionic) solution depends on :
 - (i) The nature of the electrolyte added
 - (ii) The size of the ions produced and their solvation
 - (iii) The nature of the solvent and its viscosity
 - (iv) Concentration of the electrolyte
 - (v) Temperature (it increases with the increase of temperature)

Section C

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

22.

- A is an organic compound with a molecular formula $C_8H_{16}O_2$. This gives a carboxylic acid (B) and alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester.
- Further, oxidation of alcohol (C) with chromic acid gives acid B. Thus, B and C must contain an equal number of carbon atoms.
- A total of 8 carbon atoms are present in compound A, each of B and C contain 4 carbon atoms.
- Again, alcohol C gives but-1-ene on dehydration. Therefore, C is of straight-chain and hence, it is butan-1-ol.
- On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid.
- Hence, the ester with molecular formula $C_8H_{16}O_2$ is butylbutanoate.
- All the given reactions can be explained by the following equations.

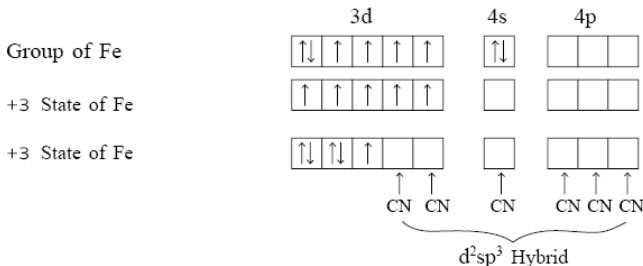


23.

The $[\text{Fe}(\text{CN})_6]^{3-}$ complex iron has +3 Oxidation state

Electrone configuration of Fe^{+3} : $[\text{Ar}] 3d^64s^2$

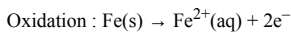
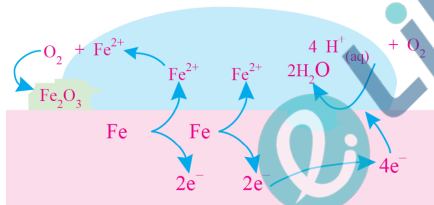
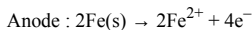
Since CN^- is the dominant ligand there is a rearrangement of six electrons in the 3d orbital, and d^2sp^3 hybridization occurs in the orbital of the metal ion.



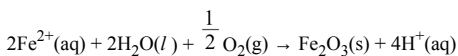
$[\text{Fe}(\text{CN})_6]^{3-}$ has 0 unpaired electrons and is diamagnetic and has complex octahedral structure.

24.

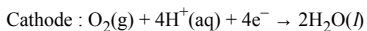
- In corrosion, a metal is oxidised by loss of electrons to oxygen and in form of oxides.
- Corrosion of iron (commonly known as rusting) occurs in presence of water and air.
- At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction.



Atmospheric oxidation :

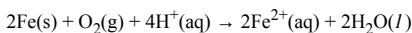


- Electrons released at anodic spot move through the metal and go to another spot on the metal, where they reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water.



$$E_{\text{H}^+ | \text{O}_2 | \text{H}_2\text{O}}^6 = 1.23 \text{ V}$$

The overall reaction being :



$$E_{(\text{cell})}^6 = 1.67\text{V}$$

- The ferrous ions are further oxidised by atmosphere oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) and with further production of hydrogen ions.

(i) "The inverse of resistivity, called conductivity (specific conductors) is represented by the symbol, κ (greek, kappa)"

➔ The SI unit of conductivity are $S\ m^{-1}$ but quite often, κ is expressed in $S\ cm^{-1}$

➔ Conductivity of a material in $S\ m^{-1}$ is its conductance when it is 1 m long and its area of cross sections 1 m^2 .

$$1\ S\ cm^{-1} = 100\ S\ m^{-1}.$$

(ii) "The resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2 ."

$$\therefore \rho = R \left(\frac{A}{l} \right)$$

➔ Its SI units are ohm metre (Ωm) and quite often its submultiple, ohm centimetre ($\Omega\ cm$) is also used.

$$1\ \Omega\ m = 100\ \Omega\ cm\ \text{or}\ 1\ \Omega\ cm = 0.01\ \Omega\ m$$

25.

➔ $W_2 = 10\ g,$ $W_1 = 250\ g$

$$M_2 = 4(C) + 7(H) + Cl + 2(O)Ka = 1.4 \times 10^{-3}$$

$$= 4(12) + 7(1) + 35.5 + 2(16)$$

$$= 122.5\ g.Mol^{-1} \qquad K_f = 1.86\ K.kg.Mol^{-1}$$

$$\Delta T_f = (?)$$

(Molality)

$$C = \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{10 \times 1000}{122.5 \times 250}$$

$$= 0.3265\ Mol/L$$

$$Ka = \frac{\alpha^2 \cdot C}{1 - \alpha}$$

$$1.4 \times 10^{-3} = \alpha^2 \cdot (0.3265)$$

$$4.287 \times 10^{-3} = \alpha^2$$

$$0.4287 \times 10^{-2} = \alpha^2$$

$$\alpha = 0.6547 \times 10^{-1}$$

$$\alpha = 0.06547$$

$$\alpha = \frac{i-1}{n-1}$$

$$0.06547 = \frac{i-1}{2-1}$$

$$i = 1.06547$$

➔ So, depression in the freezing point is

$$\Delta T_f = i \cdot K_f \cdot m$$

$$= (1.06547)(1.86)(0.3265)$$

$$= 0.647\ K$$

26.

➔ A → product

$$\text{here, } T_1 = 10\ ^\circ C = 283\ K$$

$$k_1 = 4.5 \times 10^3\ s^{-1}$$

$$E_a = 60\ kJ\ mol^{-1} = 60000\ J\ mol^{-1}$$

$$k_2 = 1.5 \times 10^4\ s^{-1}$$

$$T_2 = ?$$

$$R = 8.314\ J\ K^{-1}\ mol^{-1}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000}{2.303 \times 8.314} \left[\frac{1}{283} - \frac{1}{T_2} \right]$$

$$0.5228 = \frac{60000}{2.303 \times 8.314} \left[\frac{1}{283} - \frac{1}{T_2} \right]$$

$$\left[\frac{1}{283} - \frac{1}{T_2} \right] = \frac{2.303 \times 8.314 \times 0.5228}{60000}$$

$$\frac{1}{283} - \frac{1}{T_2} = 0.0001668$$

$$\frac{1}{T_2} = \frac{1}{283} - 0.0001668$$

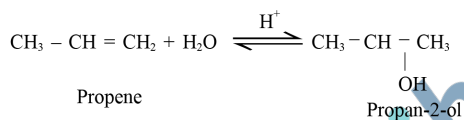
$$\frac{1}{T_2} = 0.003534 - 0.0001668 = 0.003367$$

$$T_2 = \frac{1}{0.003367} = 297.00 \text{ K}$$

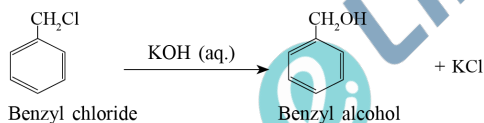
$$T_2 = 297 - 273 = 24 \text{ }^\circ\text{C}$$

27.

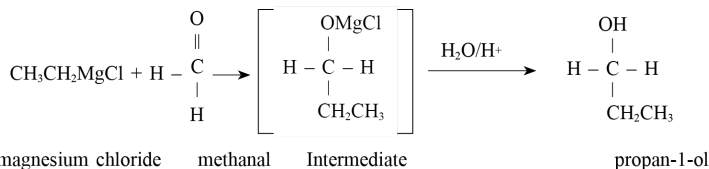
➔ (i) Propene → Propan-2-ol



➔ (ii) Benzyl chloride → Benzyl alcohol



➔ (iii) Ethyl magnesium chloride → Propan-1-ol.



➔ (iv) Methyl magnesium bromide → 2-Methylpropan-2-ol

