SOLUTIONS

1. Colligative properties are properties of solution which depend on the number of solute particles in the solution irrespective of their nature.
   a) Name the four important colligative properties. (2)
   b) What happens to the colligative properties when ethanoic acid is treated with benzene? Give reason. (2)
   [MARCH 2010]

   Ans: a) The important colligative properties are Relative lowering of vapour pressure, Elevation of boiling point, Depression of freezing point, Osmotic pressure.
   b) Ethanoic acid (acetic acid) dimerises in benzene. So the no. of particles decreases and hence the colligative properties decreases.
2. Colligative properties can be used to determine the molar mass of solutes in solutions.
   a) What do you mean by colligative properties? (1)
   b) For determining the molecular mass of polymers, osmotic pressure is preferred to other properties. Why? (1)
   c) For intravenous injections only solutions with osmotic pressure equal to that of 0.9% NaCl solution is used. Why? (2) *[MARCH 2011]*

   Ans: a) These are properties which depend on the number of solute particles and not on their nature.
   b) Polymers have poor solubility and so their solution is very dilute. The magnitude of osmotic pressure is large even for very dilute solutions. So osmotic pressure measurement is used for the determination of their molar mass.
   c) This is because our blood cells are isotonic with 0.9% (mass/volume) NaCl solution. So osmosis does not occur if we place the blood cells in this solution. (If the blood cells are placed in NaCl solution with higher or lower concentrations than 0.9 %, they would shrink or swell).
3. Relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure are important colligative properties of dilute solutions.
   a) Relative lowering of vapour pressure of an aqueous dilute solution of glucose is 0.018. What is the mole fraction of glucose in the solution? (1)
   b) An aqueous dilute solution of a non-volatile solute boils at 373.052K. Find the freezing point of the solution. For water K_b = 0.52 K kgmol^{-1} and K_f = 1.86 K kgmol^{-1}. Normal boiling point of water = 373K and normal freezing point = 273K. (3) *[SAY 2011]*

   Ans: a) Relative lowering of Vapour pressure ($\Delta P / P_1^0$) = x_2, the mole fraction of the solute.
   Here relative lowering of vapour pressure of glucose = 0.018. So its mole fraction = 0.018.
   b) Here b.p of solution (T_b) = 373.052 K and that of water (T_b^0) = 373 K.
   Elevation of b.p, $\Delta T_b = T_b - T_b^0 = 373.052 - 373 = 0.052$ K
   We know that, $\Delta T_b = K_b.m$
   So, molality, $m = \Delta T_b / K_b = 0.052/0.52 = 0.1$
   The depression in freezing point, $\Delta T_f = K_f.\ m = 1.86 \times 0.1 = 0.186$ K
   Also, $\Delta T_f = T_f - T_f^0$
   So, freezing point of the solution (T_f) = $\Delta T_f + T_f^0 = 0.186 + 273 =$ 273.186 K
4. Vapour pressure of a solution is different from that of pure solvent.
   i) Name the law which helps us to determine partial vapour pressure of a volatile component in a solution. (½)
   ii) State the above law. (1)
   iii) Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298K are 200 mm of Hg and 415 mm of Hg respectively. Calculate the vapour pressure of solution prepared by mixing 24g of chloroform and 17g of dichloromethane at 298K. (2½) *[MARCH 2012]*

Ans: i) Raoult's law

ii) The law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction present in solution.

iii) Let $CHCl_3$ be the component 1 and CH_2Cl_2 be the component 2.

Then vapour pressure of pure chloroform (P_1^0) = 200 mm of Hg and vapour pressure of pure CH_2Cl_2 (P_2^0) = 415 mm of Hg.

Mass of Chloroform (w_1) = 24 g

Molar mass of Chloroform, $CHCl_3$ (M_1) = 12 + 1 + 3 x 35.5 = 119.5 g/mol

No. of moles of Chloroform (n_1) = w_1/M_1 = 24/119.5 = 0.2 mol

Mass of dichloromethane (w_2) = 17 g

Molar mass of dichloromethane, CH_2Cl_2 (M_2) = 12 + 2 x 1 + 2 x 35.5 = 85 g/mol

No. of moles of CH_2Cl_2 (n_2) = w_2/M_2 = 17/85 = 0.2 mol

Mole fraction of CH_2Cl_2 (x_2) = $n_2/(n_1+n_2)$ = 0.2/(0.2+0.2) = 0.5

Total pressure of the solution = $P_1^0 + (P_2^0 - P_1^0).x_2$ = 200 + (415-200) x 0.5 = 307.5 mm of Hg

[Or, find out x_1 also and then calculate P_1 ($P_1 = P_1^0.x_1$), P_2 ($P_2 = P_2^0.x_2$) & $P_{Total} = P_1 + P_2$]

5. Colligative properties are properties of solution which depend on the number of solute particles in the solution.
   i) Write the names of four important colligative properties. (2)
   ii) The value of van't Hoff factor 'i', for aqueous KCl solution is close to 2, while that for ethanoic acid in benzene is nearly 0.5. Give reason. (2) *[SAY 2012]*

Ans: i) Relative lowering of vapour pressure, Elevation of boiling point, Depression of freezing point, Osmotic pressure.

ii) KCl dissociates in aqueous solution. So the no. of solute particles gets doubled and hence 'i' is close to 2. While ethanoic acid dimerises in benzene. So the no. of particles gets halved and hence 'i' is nearly 0.5.

6. Elevation of boiling point is a colligative property.
   i) What are colligative properties? (1)
   ii) Elevation of boiling point (ΔT_b) is directly proportional to molality (m) of solution. Thus $\Delta T_b = K_b.m$, K_b is called molal elevation constant. From the above relation derive an expression to obtain molar mass of the solute.(1)
   iii) The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11K. Calculate the molar mass of the solute. K_b for benzene is 2.53 K kg mol^{-1}. (1) *[MARCH 2013]*

Ans: i) These are properties which depend on the number of solute particles and not on their nature.

ii) Given $\Delta T_b = K_b.m$

But molality $m = \frac{w_2 \times 1000}{M_2 \times w_1}$

Therefore, $\Delta T_b = \frac{K_b.\, w_2 \times 1000}{M_2.w_1}$

Or, $\Delta T_b = \frac{1000 K_b.w_2}{w_1.M_2}$ *Where w_1 = mass of solvent, w_2 = mass of solute, M_2 = molar mass of solute. By using this equation, we can calculate the molar mass of unknown solute.*

iii) We know that $\Delta T_b = \frac{1000\ K_b\ .\ w_2}{w_1.\ M_2}$

Here w_2 = 1.80 g, w_1 = 90g, $\Delta T_b = T_b - T_b^0$ = 354.11 – 353.23 = 0.88 K, K_b = 2.53 K kg/mol, M_2 = ?

On substituting in the above equation, we get

$$0.88 = \frac{1000 \times 2.53 \times 1.80}{90 \times M_2}$$

$$\text{So, } M_2 = \frac{1000 \times 2.53 \times 1.8}{90 \times 0.88} = 57.5 \text{ g/mol}$$

7. Liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.
   a) State Raoult's law. (1)
   b) What are ideal solutions? (1)
   c) Write any two properties of ideal solutions. (1)
   d) What type of deviation is shown by a mixture of chloroform and acetone? Give reason. (1) *[SAY 2013]*

Ans: a) The law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction present in solution.

b) These are solutions which obey Raoult's law at all concentrations.
E.g. A mixture of benzene and toluene

c) For an ideal solution, $P_1 = P_1^0 x_1$, $P_2 = P_2^0 x_2$, $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$

d) Negative deviation. Chloroform can form hydrogen bond with acetone. So the solute – solvent interaction increases and hence the vapour pressure decreases.

8. Osmotic pressure is a colligative property and it is proportional to the molarity of the solution.
   a) What is osmotic pressure? (1)
   b) Molecular mass of NaCl determined by osmotic pressure measurement is found to be half of the actual value. Account for it? (1)
   c) Calculate the osmotic pressure exerted by a solution prepared by dissolving 1.5 g of a polymer of molarmass 185000 in 500ml of water at 37^0C. (R = 0.0821 L atm/K/mol) (2) *[March 2014]*

Ans: a) It is the excess pressure that must be applied on solution side to stop osmosis. Or, it is the pressure that just stops the flow of solvent molecules through a semi-permeable membrane.

b) This is because NaCl dissociates in aqueous solution. Hence the no. of particles gets doubled and colligative property (osmotic pressure) becomes halved.

c) Here $w_2 = 1.5$ g, $R = 0.0821$ L atm/K/mol, $M_2 = 185000$, $T = 37^0C = 37 + 273 = 310K$ and $V = 500$ mL $= 0.5$ L
We Know that, Osmotic pressure, $\pi = \frac{w_2RT}{M_2V} = \frac{1.5 \times 0.0821 \times 310}{185000 \times 0.5} = 4.13 \times 10^{-4}$ atm

9. Molarity (M), molality (m) and mole fraction (x) are some methods for expressing concentration of solutions.
   a) Which of these are temperature independent? (1)
   b) Define mole fraction? (1)
   c) A mixture contains 3.2g methanol (molecular mass = 32u) and 4.6g ethanol (molecular mass = 46u). Find the mole fraction of each component. (2) *[SAY 2014]*

Ans: a) Molality and mole fraction.

b) Mole fraction is the ratio of the number of moles of a particular component to the total number of moles of solution.

c) Let methanol be component 1 and ethanol be component 2.
Then $w_1 = 3.2$ g, $M_1 = 32$ u, $w_2 = 4.6$ g and $M_2 = 46$u.
No. of moles of methanol $(n_1) = w_1/M_1 = 3.2/32 = 0.1$ mol
No. of moles of ethanol $(n_2) = w_2/M_2 = 4.6/46 = 0.1$ mol
*Mole fraction of methanol $(x_1) = n_1/(n_1+n_2) = 0.1/(0.1+0.1) =$ **0.5***
*Mole fraction of ethanol $(x_2) = 1 - x_1 = 1 - 0.5 =$ **0.5***

10. a) Among the following, which is not a colligative property?

i) Osmotic pressure ii) Elevation of boiling point iii) Vapour pressure iv) Depression of freezing point (1)

b) i) 200 cm^3 of aqueous solution of a protein contains 1.26 g of protein. The osmotic pressure of the solution at 300 K is found to be 8.3 x 10^{-2} bar. Calculate the molar mass of protein. (R = 0.083 $LbarK^{-1}mol^{-1}$) (2)

ii) What is the significance of van't Hoff factor? (1) *[March 2015]*

Ans: a) iii) Vapour pressure

b) i) Here w_2 = 1.26 g, R = 0.083 L bar/K/mol, π = 8.3 x 10^{-2} bar, T = 300K & V= 200 cm^3 = 0.2 L

We Know that, Molar mass of solute, $M_2 = \frac{w_2RT}{\pi V} = \frac{1.26 \times 0.083 \times 300}{8.3 \times 10^{-2} \times 0.2}$ = 1890 g/mol

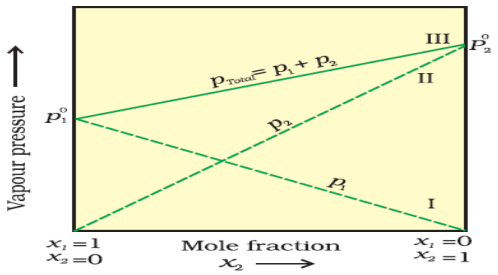
ii) van't Hoff factor is used to correct the abnormal molar mass of solute if there is association or dissociation of particles.

11. a) Draw a vapour pressure curve, by plotting vapour pressure against mole fraction of an ideal solution of two components A and B. indicate partial vapour pressure of A and B (P_A and P_B) and the total vapour pressure (P_{Total}). (2)

b) What is an ideal solution? (1)

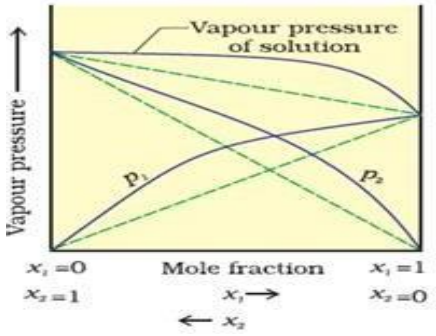
c) Modify the above plot for non-ideal solution showing positive deviation. (Draw the above plot once again and modify.) (1) *[SAY 2015]*

Ans: a)



b) A solution which obeys Raoult's law at all concentrations is called ideal solution.

c)



12. a) Number of moles of the solute per kilogram of the solvent is:

(a) Mole fraction (b) Molality (c) Molarity (d) Molar mass (1)

(b) 'The extent to which a solute is dissociated or associated can be expressed by Van't Hoff factor.' Substantiate the statement. (1)

(c) The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A nonvolatile, non-electrolyte solid weighing 0.5 g when added to 39 g of benzene (molar mass 78 g mol^{-1}), vapour pressure becomes 0.845 bar. What is the molar mass of the solid substance? (2) *[March 2016]*

Ans: a) Molality

b) van't Hoff factor, i = Total number of moles of particles after association/dissociation / Number of moles of particles before association/dissociation

If the value of i < 1, association occurs and if the value of i > 1, dissociation occurs.

c) We know that, $\frac{\Delta P}{P_1^0} = \frac{w_2 \times M_1}{w_1 \times M_2}$

Here vapour pressure of pure solvent benzene (P_1^0) = 0.850 bar, Mass of benzene (w_1) = 39 g, mass of solute (w_2) = 0.5 g, molar mass of benzene (M_1) = 78 g/mol and vapour pressure of solution (P_1) = 0.845 bar

$\Delta P = P_1^0 - P_1 = 0.850 - 0.845 = 0.005$ bar

On substituting in the above equation, we get,

$$\frac{0.005}{0.850} = \frac{0.5 \times 78}{39 \times M_2}$$

So, $M_2 = \frac{0.5 \times 78 \times 0.85}{0.005 \times 39} = 170$ *g/mol*

13. Osmotic pressure is a colligative property.
    a) What is osmotic pressure? (1)
    b) 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40K. The freezing point depression constant of benzene is 5.12 K kg/mol. Find the molar mass of the solute. (3) *[SAY 2016]*

Ans: a) It is the excess pressure that must be applied on solution side to prevent osmosis.

b) We know that $\Delta T_f = \frac{1000 K_f . w_2}{w_1 . M_2}$

Here w_2 = 1.00 g, w_1 = 50g, ΔT_f = 0.40 K, K_f = 5.12 K kg/mol, M_2 = ?

On substituting in the above equation, we get

$$0.4 = \frac{1000 \times 5.12 \times 1}{50 \times M_2}$$

So, $M_2 = \frac{1000 \times 5.12 \times 1}{50 \times 0.4} = 256$ *g/mol*

14. a) Henry's law is related to solubility of a gas in liquid.
    (i) State Henry's law. (2)
    (ii) Write any two applications of Henry's law. (2)
    b) 1000cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300K is found to be 2.57 x 10^{-3} bar. Calculate the molar mass of the protein. (R = 0.083 L bar/K/mol). (2) *[March 2017]*

Ans: a) (i) Henry's law states that at constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

Or, at constant temperature, the partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution.

Mathematically, $p = K_H.x$ (where p is the partial pressure, x is the mole fraction and K_H is the Henry's law constant).

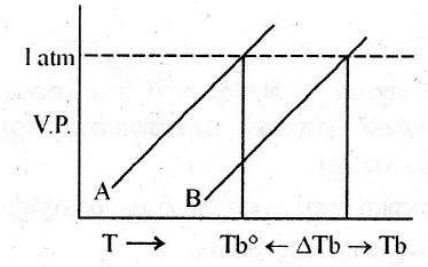
(ii) In the preparation of soda water the bottle is sealed at high pressure, a condition known as Bends in Scuba divers, a medical condition known as Anoxia in people living at high altitudes or climbers. (Any 2 applications)

(b) Given V = 1000 cm^3 = 1 L, w_2 = 1.26 g, π = 2.57 x 10^{-3} bar, T = 300 K, R = 0.083 LbarK^{-1}mol^{-1}

$$M_2 = \frac{w_2 RT}{\pi V} = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 1} = 12.2077 \times 10^3 \text{ g/mol}$$

15. a) The mole fraction of water in a mixture containing equal number of moles of water and ethanol is:
    i) 1 ii) 0.5 iii) 2 iv) 0.25 (1)

    b) The following are the vapour pressure curves of a pure solvent and a solution of a non-volatile solute in it.



    Based on the above curves answer the following questions.

    i) What do the curves A and B indicates? (1)

    ii) Explain why the value of T_b is greater than that of T_b^0. (2) *[SAY 2017]*

    Ans: a) 0.5

    b) i) A – Pure solvent and B – Solution

    ii) Since the solute is non-volatile, the vapour pressure of solution is always less than that of the pure solvent. So it boils at higher temperature.

16. A solution contains 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. (2)

    Ans: Here the two solutions have same osmotic pressure. So they are isotonic. Hence $\pi_1 = \pi_2$.

    We know that $\pi = nRT/V$

    Therefore, $\pi_1 = n_1RT/V$

    And $\pi_2 = n_2RT/V$

    Since $\pi_1 = \pi_2$, it follows that $n_1 = n_2$ (at constant temperature and volume)

    Or, $w_1/M_1 = w_2/M_2$ (Here 1 indicates urea and 2 indicates glucose)

    Or, $15/60 = w_2/180$

    So, $w_2 = 15x180/60 = 45g$

    i.e. Mass of glucose = 45g

17. Define minimum boiling azeotropes with example. (2) *[March 2018]*

    Ans: The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a particular composition. E.g. 95% ethanol solution by volume.

18. Draw the vapour pressure-mole fraction curve for a non-ideal solution having positive deviation, if A and B are the two volatile components. (2)

    Ans: Refer the Answer of Question no. 11 (c)

19. Calculate the depression in freezing point of a 0.2 molal solution if k_f for water is 1.86 K kg mol^{-1}. (2) *[SAY 2018]*

    We know that, $\Delta T_f = kf.m = 1.86 \times 0.2 = 0.372$ K

20. What is reverse osmosis? Write ally one of its applications. (2)

    Ans: If a pressure larger than the osmotic pressure is applied to the solution side, the direction of osmosis gets reversed (i.e. now the pure solvent flows out of the solution through the semi permeable membrane). This phenomenon is called reverse osmosis.

    It is used in desalination of sea water.

21. A 5% solution (by mass) of cane sugar ($C_{12}H_{22}O_{11}$)) in water has a freezing point of 271K. Calculate the freezing point of 5% (by mass) solution of glucose ($C_6H_{12}O_6$) in water. Freezing point of pure water is 273.15 K. (3)

    [March 2019]

Ans: We know that $\Delta T_f = \frac{1000\ K_f . w_2}{w_1 . M_2}$

5% cane sugar ($C_{12}H_{22}O_{11}$) solution by mass means 5g cane sugar is present in 100g solution.
So, Mass of cane sugar (w_2) = 5g, Mass of solvent, water (w_1) = 100 – 5 = 95g
Molar mass of cane sugar (M_2) = 342 g/mol, freezing point of solution (T_f) = 271 K, freezing point of pure water (T_f^0) = 273.15 K.
So $\Delta T_f = T_f^0 - T_f = 273.15 - 271 = 2.15\ K$

$K_f = \frac{\Delta T_f . w_1 . M_2}{1000 \times w_2} = \frac{2.15 \times 95 \times 342}{1000 \times 5} = 13.97\ K/molal$

5% glucose solution by mass means 5g glucose is present in 100g solution.
So, Mass of glucose (w_2) = 5g, Mass of slovent (w_1) = 100 – 5 = 95g
Molar mass of glucose (M_2) = 180g/mol, K_f = 13.97 K/molal
Therefore, $\Delta T_f = \frac{1000 \times 13.97 \times 5}{95 \times 180} = 4.085\ K$
Also, $\Delta T_f = T_f^0 - T_f$
Therefore, freezing point of solution, $T_f = T_f^0 - \Delta T_f = 273.15 - 4.085 = 269.065\ K$

22. Which of the following is not a colligative property?
(a) Osmotic pressure (b) Vapour pressure (c) Elevation of boiling point (d) Depression of freezing point (1)
Ans: (b) Vapour pressure

23. What is meant by positive and negative deviation from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviation ? (3) *[SAY 2019]*
Ans: These are related to non-ideal solution. Positive deviation from Raoult's law means their actual vapour pressure is greater than that predicted by Raoult's law. This is because here the solute-solvent interactions are weaker than solute-solute and solvent-solvent interactions. For such solutions, $\Delta_{mix}H$ is positive. i.e. on mixing the components, heat is absorbed.
For Negative deviation from Raoult's law, the actual vapour pressure is less than that predicted by Raoult's law. Here the solute-solvent interactions are stronger than solute-solute and solvent-solvent interactions. For such solutions, $\Delta_{mix}H$ is negative. i.e. on mixing the components, heat is evolved.

24. For ethanol-acetone mixture solute-solvent interaction is weaker than solute-solute and solvent-solvent interaction.
a) Does this solution obey Raoult's law? (1)
b) Give the vapour pressure-mole fraction graph for this solution. (2) *[March 2020]*
Ans: a) No. This mixture shows positive deviation from Raoult's law.
b) Refer the answer of question no. 11 (c)

25. Complete the table by giving the value of Van't Hoff factor 'I' for complete dissociation of solute. (2)

Salt	Van't Hoff factor 'i' for complete dissociation of solute
NaCl	
$Al(NO_3)_3$	
K_2SO_4	
$Al_2(SO_4)_3$	

Ans:

Salt	*NaCl*	*$Al(NO_3)_3$*	*K_2SO_4*	*$Al_2(SO_4)_3$*
Van't Hoff factor 'i'	*2*	*4*	*3*	*5*

26. (a) You are given a sample of a polymer and asked to find its molar mass. Which colligative will be more effective to find it? (1)

(b) Give reason for your answer. (1)

Ans: (a) Osmotic Pressure

(b) Polymers are very less soluble, but the value of osmotic pressure is large even for very dilute solutions. So osmotic pressure measurement is used to determine the molar mass.

27. (a) Define molal depression constant. (1)

(b) 0.4 g of non-electrolyte dissolved in 20 g of benzene lowers its freezing point by 0.75 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute. (2) *[SAY 2020]*

Ans: (a)It is the depression of freezing point for 1 molal solution.

(b) We know that $\Delta T_f = \frac{1000\ K_f . w_2}{w_1 . M_2}$

Here $w_2 = 0.4$ g, $w_1 = 20$g, $\Delta T_f = 0.75$ K, $K_f = 5.12$ K kg/mol, $M_2 = ?$

On substituting in the above equation, we get

$0.75 = \frac{1000 \times 5.12 \times 0.4}{20 \times M_2}$

So, $M_2 = \frac{1000 \times 5.12 \times 0.4}{20 \times 0.75} = 136.53$ g/mol

28. Mixture of two liquids A and B form an ideal solution. Draw the vapour pressure- composition curve for this solution. (2)

Ans: Refer the answer of question no. 11 (a)

29. State Henry's Law. Give two applications of it. (3)

Ans: Refer the answer of question no. 14 (a)

30. (i) The vapour pressure of pure liquids A and B are 400 mm of Hg and 600 mm of Hg respectively. Calculate vapour pressure of the solution in which mole fraction of B is 0.4. (2)

(ii) Which of the following is true for an ideal solution?

(A) $\Delta H_{mix} > 0$ (B) $\Delta H_{mix} = 0$ (C) $\Delta V_{mix} > 0$ (D) $\Delta H_{mix} < 0$ (1)

Ans: (i) $P_{Total} = P^0_A + (P^0_B - P^0_A)x_B$

Here $P^0_A = 400$ mm of Hg, $P^0_B = 600$ mm of Hg and $x_B = 0.4$

So, $P_{Total} = 400 + (600 - 400) \times 0.4 =$ ***480 mm of Hg***

OR, Since $x_B = 0.4$, $x_A = 1 - x_B = 1 - 0.4 = 0.6$

$P_A = P^0_A . x_A = 400 \times 0.6 = 240$ mm of Hg

$P_B = P^0_B . x_B = 600 \times 0.4 = 240$ mm of Hg

$P_{Total} = P_A + P_B = 240 + 240 =$ ***480 mm of Hg***

(ii) $\Delta H_{mix} = 0$

31. (i) What are colligative properties ? (2)

(ii) 400 cm^3 of an aqueous solution of a protein contain 1.26 g of the protein. The osmotic pressure of such solution at 300K is found to be 2.57×10^{-4} atm. Calculate molar mass of protein. (R = 0.0821 L $atmK^{-1}$ mol^{-1}). (2) *[March 2021]*

Ans: (i) These are properties which depend on the number of solute particles and not on their nature.

(ii) Here $w_2 = 1.26$ g, $R = 0.0821$ L atm/K/mol, $\pi = 2.57 \times 10^{-4}$ atm, $T = 300$K & $V = 400\ cm^3 = 0.4$ L

We Know that, Molar mass of solute, $M_2 = \frac{w_2 RT}{\pi V} = \frac{1.26 \times 0.0821 \times 300}{2.57 \times 10^{-4} \times 0.4} =$ ***30.19×10^4 g/mol***

32. What is reverse osmosis? Mention any one of its application. (2)

Ans: Refer the answer of question no. 20

33. (i) State Raoult's law. (1)

(ii) What is meant by positive deviation of solutions from ideal behaviour? (1)

(iii) What are Azoetropes ? (1)

Ans: (i) Refer the answer of question no. 4 (ii)

(ii) Refer the answer of question no. 23

(iii) Binary mixtures having same composition in liquid phase and vapour phase and boils at a constant temperature are called azeotropes.

34. Boiling point of water at 750 mm Hg is 99.63 ^{0}C. How much sucrose ($C_{12}H_{22}O_{11}$) is to be added to 500g of water such that it boils at 100^{0}C ? (K_b = 0.52 K kg mol^{-1}) (3)

Ans: We know that $\Delta T_b = \frac{1000\ K_b . w_2}{w_1 . M_2}$

Here $w_1 = 500$ g, $\Delta T_b = T_b - T_b^0 = 100 - 99.63 = 0.37^0$C, $K_b = 0.52$ K kg/mol, $M_2 = 342$ g/mol, $w_2 = ?$

On substituting in the above equation, we get

$0.37 = \frac{1000 \times 0.52 \times w_2}{500 \times 342}$

So, $w_2 = \frac{0.37 \times 500 \times 342}{1000 \times 0.52} =$ ***121.67g***

35. (i) State Henry's law. (1)

(ii) Mention two applications of Henry's law. (2)

(iii) Aquatic organisms are more comfortable in cold water. Why ? (1) *[SAY 2021]*

Ans: (i) & (ii) Refer the answer of question no. 14 (a)

21 When temperature decreases, the solubility of oxygen in water increases. Or, in cold water, the amount of dissolved oxygen is greater. So, aquatic organisms are more comfortable in cold water.

36. Two solutions having same osmotic pressure at a given temperature are called _____. (1)

Ans: Isotonic solutions

37. State Henry's law and mention any one of its application. (2)

Ans: Refer the answer of question no. 14 (a)

38. 18g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a sauce pan. At what temperature will water boil at 1.013 bar? (K_b for water is 0.52 Kkgmol^{-1}, boiling point of water = 373.15 K) (3) *[March 2022]*

Ans: We know that $\Delta T_b = \frac{1000\ K_b . w_2}{w_1 . M_2}$

Here $w_2 = 18$ g, $w_1 = 1$ kg $= 1000$g, $K_b = 0.52$ K kg/mol, $M_2 = 180$, $T_b^0 = 373.15$ K, $\Delta T_b = ?$, $T_b = ?$

On substituting in the above equation, we get

$\Delta T_b = \frac{1000 \times 0.52 \times 18}{1000 \times 180} = 0.052$ K

Also $\Delta T_b = T_b - T_b^0$

i.e. $0.052 = T_b - 373.15$

So, $T_b = 0.052 + 373.15 =$ ***373.202 K***

39. The solutions having equal osmotic pressure at a given temperature is called _____. (1)

Ans: Isotonic solutions

40. (i) State Raoult's Law. (1)

(ii) Draw a plot of vapour pressure and mole fraction of an ideal solution at constant temperature. (1)

Ans: Refer the answer of question no. 7 (a) and 11 (a)

41. (i) Define molarity. (1)

(ii) Calculate the molarity of a solution containing 10g of NaOH in 450 ml solution. (2) *[SAY 2022]*

Ans: (i) Molarity is the no. of moles of solute present per litre of the solution.

(ii) Here mass of NaOH = 10g

Molar mass of NaOH = 40 g/mol

$$\text{No. of moles of NaOH} = \frac{\text{Mass of NaOH}}{\text{Molar mass of NaOH}} = \frac{10}{40} = 0.25 \text{ mol}$$

Volume of solution = 450 mL = 0.45L

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}} = \frac{0.25}{0.45} = \mathbf{0.556\ M}$$

42. State Henry's law. Write any one application of it. (2)

Ans: Refer the answer of Question number 14 (a)

43. What are Ideal Solutions ? Give one example. (2)

Ans: Refer the answer of Question number 7 (b)

44. (i) What are colligative properties ? (1)

(ii) Write any two colligative properties. (1)

(iii) What is reverse osmosis ? Mention one important practical utility of reverse osmosis. (2) *[March 2023]*

Ans: Refer the answer of Question number 2 (a), 1 (a) and 20.

45. What type of deviation from Raoult's law is exhibited by a mixture of phenol and aniline? Justify your answer. (2)

Ans: Negative deviation.

Phenol forms stronger inter molecular hydrogen bonding with aniline. So the number of particles entering to vapour phase decreases and hence the vapour pressure of the solution is less than that predicted by Raoult's law.

46. State Henry's law. Mention one application of Henry's law. (2)

Ans: Refer the answer of Question number 14 (a)

47. (i) Define colligative properties ? (1)

(ii) Mention four colligative properties. (2)

(iii) Which colligative property measurement is the best method for determining the molecular mass of proteins? (1) *[SAY 2023]*

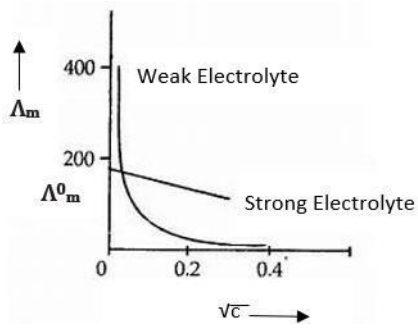
Ans: (i) & (ii) Refer the answer of Question number 1 (a) and 2 (a)

(iii) Osmotic pressure

##########

ELECTROCHEMISTRY

1. The graphs showing the variation of molar conductance with concentration for weak and strong acids are given.



a) Explain the Debye-Huckel-Onsagar equation? (1)

b) What is molar conductance? (1)

c) Calculate the molar conductance at infinite dilution of NH_4OH.

Given that Λ^0_m for NaCl, NaOH and NH_4Cl are 126.4, 248.1 and 129.8 $ohm^{-1}cm^2mol^{-1}$. (2) *[March 2008]*

Ans: a) : $\Lambda_m = \Lambda^0_m - AVc$

b) Molar conductivity is the conductivity of 1 mole of an electrolytic solution kept between two electrodes of a conductivity cell with unit area of cross section and at a distance of unit length.

c) Given Λ^0m (NaCl) = 126.4 Scm^2mol^{-1}, Λ^0m (NaOH) = 248.1 Scm^2mol^{-1} and Λ^0m (NH_4Cl) = 129.8 Scm^2mol^{-1}

Applying Kohlrausch's law, $\Lambda^0m(NH_4OH) = \Lambda^0m$ (NaOH) + Λ^0m (NH_4Cl) – Λ^0m (NaCl)

*= 248.1 + 129.8 – 126.4 = **251.5 Scm^2mol^{-1}***

2. Certain Galvanic cells are designed to convert the energy of combustion of fuels directly into electrical energy.

a) Name the above type of Galvanic cells. (½)

b) Give an example for the above cell. (½)

c) Represent the reactions taking place at anode and cathode of the above cell. (2)

d) Mention any two advantages of the above cell. (1) *[March 2009]*

Ans: a) Fuel cells

b) H_2 - O_2 fuel cell

c) Anode reaction: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Cathode reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

d) The advantages of fuel cell are:

i) The cell works continuously as long as the reactants are supplied.

ii) It has higher efficiency as compared to other conventional cells.

iii) It is eco-friendly (i.e. pollution free) since water is the only product formed.

iv) Water obtained from $H_2 – O_2$ fuel cell can be used for drinking. [Any 2 required]

3. Lead storage cell is the commonly used secondary cell in automobiles.

a) What is a secondary cell? (1)

b) What are the anode and cathode of the cell? (1)

c) Write down the reactions at anode and cathode during discharging of the cell? (2) *[March 2010]*

Ans: a) These are cells that can be recharged and reused. Here the cell reaction can be reversed.

b) Anode: Lead, Cathode: A grid of lead packed with PbO_2.

c) Anode reaction: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode reaction: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$.

4. From the position of elements in the electrochemical series, Cu can displace Ag from $AgNO_3$ solution.
   a) Represent the cell constructed with Cu and Ag electrodes. (1)
   b) Write down the cell reaction taking place at the anode and the cathode. (2)
   c) Write the Nernst equation for the above cell reaction. (1) *[March 2010]*

Ans: a) $Cu/Cu^{2+}//Ag^+/Ag$

b) Anode reaction: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode reaction: $Ag^+(aq) + e^- \rightarrow Ag(s)$

c) The net reaction for the above cell is: $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

5. The standard electrode potentials of some electrodes are given below:
   $E^0(Zn^{2+}/Zn) = -0.76$ V, $E^0(Cu^{2+}/Cu) = 0.34$ V, $E^0(Ag^+/Ag) = 0.8$ V, $E^0(H^+/H_2) = 0$ V.
   a) Can $CuSO_4$ solution be kept in silver vessel? (½)
   b) Zn or Cu, which can displace hydrogen from dil. H_2SO_4? (½)
   c) What is the reaction taking place at SHE when it is connected with Ag^+/Ag electrode to form a galvanic cell? (1)
   d) Find the value of Kc (equilibrium constant) in the Daniel cell at 298K. (2) *[SAY 2011]*

Ans: a) Yes

b) Zn (Since Zn lies above H in activity series, while Cu lies below H)

c) $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ [Oxidation occurs at SHE since it has lower $E^0_{el.}$ value than Ag]

d) At 298K, $E^0_{cell} = \frac{0.0591}{n} \log Kc$

For Daniel cell, $n = 2$ and $E^0_{cell} = 1.1$ V

So, $\log Kc = E^0_{cell} \times n/0.0591 = 1.1 \times 2/0.0591 = 37.22$

$Kc = \text{Anti-log}(37.22) = 1.65 \times 10^{37}$

6. The limiting molar conductivity of an electrolyte is obtained by adding the limiting molar conductivities of cation and anion of the electrolyte.
   a) Name the above law. (½)
   b) What is meant by limiting molar conductivity? (½)
   c) Explain how conductivity measurements help to determine the ionisation constant of a weak electrolyte like acetic acid. (1)
   d) Explain the change of conductivity and molar conductivity of a solution with dilution? (2) *[March11]*

Ans: a) Kohlrausch's law

b) Molar conductivity at zero concentration or infinite dilution is called limiting molar conductivity.

c) By knowing the molar conductivity at a particular concentration ($\lambda^c m$) and limiting molar conductivity ($\lambda^0 m$), we can calculate the dissociation constant of a weak acid by the equation;

$$Ka = \frac{c\,(\Lambda^{C}m/\Lambda^{0}m)^2}{1-(\Lambda^{C}m/\Lambda^{0}m)}$$

d) For both strong and weak electrolytes, conductivity always decreases with dilution. This is because as dilution increases, the number of ions per unit volume decreases and hence the conductivity decreases. The molar conductivity increase with dilution for both strong and weak electrolytes. This is due to the increase in ionic mobility for strong electrolytes and increase in degree of dissociation for weak electrolytes.

7. Leclanche cell, Lead storage cell and Fuel cell are galvanic cells having different uses.
   a) Among these, Leclanche cell is a primary cell and lead storage cell is a secondary cell. Write any 2 differences between primary cell and secondary cell. (2)
   b) What is a fuel cell? (1)
   c) Write the overall cell reaction in $H_2 - O_2$ fuel cell? (1) *[March 2012]*

Ans: a) Primary cell cannot be recharged or reused, while secondary cell can. In primary cell, the cell reaction cannot be reversed but in secondary cell, the cell reaction can be reversed.

b) Fuel cells are galvanic cells which convert the energy of combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy.

c) $2H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$

8. Daniel cell is a galvanic cell made of Zn and Cu electrodes.
   i) Write anode and cathode reactions in Daniel cell? (1)
   ii) Nernst equation for the electrode reaction $M^{n+} + ne^- \rightarrow M$ is:

$E_{M^{n+}/M} = E^0_{M^{n+}/M} - (2.303RT/nF)\log 1/[M^{n+}]$. Derive Nernst equation for Daniel cell. (3) *[March 2012]*

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

Cathode reaction: $Cu^{2+} + 2e^- \rightarrow Cu(s)$

ii) For Daniel cell, the electrode potentials are given as:

$$E_{(Cu^{2+}/Cu)} = E^0_{(Cu^{2+}/Cu)} + \frac{RT}{2F} \ln [Cu^{2+}] \quad \text{(For cathode)}$$

$$E_{(Zn^{2+}/Zn)} = E^0_{(Zn^{2+}/Zn)} + \frac{RT}{2F} \ln [Zn^{2+}] \quad \text{(For anode)}$$

The cell potential, $E_{cell} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$

$$= \{E^0_{(Cu^{2+}/Cu)} + \frac{RT}{2F} \ln [Cu^{2+}]\} - \{E^0_{(Zn^{2+}/Zn)} + \frac{RT}{2F} \ln [Zn^{2+}]\}$$

$$= [E^0_{(Cu^{2+}/Cu)} - E^0_{(Zn^{2+}/Zn)}] + \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

Or,

$$E_{cell} = E^0_{cell} + \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

On changing the base of logarithm, we get

$$E_{cell} = E^0_{cell} + \frac{2.303RT}{2F} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

On substituting the values of R (8.314 $JK^{-1}\,mol^{-1}$), F (96500 C mol^{-1}) at 298K, the above equation becomes,

$$E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

9. With decrease in concentration of an electrolytic solution, conductivity (k) decreases and molar conductivity (Λ_m) increases.
   i) Write the equation showing the relationship between conductivity and molar conductivity. (1)

ii) How will you account for the increase in molar conductivity with decrease in concentration? (1½)

iii) Limiting molar conductivity (Λ^0_m) of a strong electrolyte can be determined by graphical extrapolation method. Suggest a method for the determination of limiting molar conductivity of a weak electrolyte, taking acetic acid (CH_3COOH) as example. (1½) *[March 2013]*

Ans: (i) Molar conductivity, λm = 1000 fi/M [Where fi is the conductivity and M is the molarity]

(ii) For strong electrolytes, as dilution increases, the force of attraction between the ions decreases and hence the ionic mobility increases. So, molar conductivity increases. For weak electrolytes, as dilution increases, the degree of dissociation increases. So the number of ions increases and hence the molar conductivity.

(iii) Limiting molar conductivity of a weak electrolyte can be determined by knowing the Λ^0m values of strong electrolytes using Kohlrausch's law. For e.g. we can determine the Λ^0m of acetic acid (CH_3COOH) by knowing the Λ^0m of CH_3COONa, NaCl and HCl as follows:

$\Lambda^0m\ (CH_3COONa) = \lambda^0CH_3COO^- + \lambda^0Na^+$ ..... (1)

$\Lambda^0m\ (HCl) = \lambda^0H+ + \lambda^0\ Cl$..... (2)

$\Lambda^0m\ (NaCl) = \lambda^0Na+ + \lambda^0Cl$..... (3)

(1) + (2) - (3) gives:

$\Lambda^0m\ (CH_3COONa) + \Lambda^0m\ (HCl) - \Lambda^0m\ (NaCl) = \lambda^0CH_3COO^- + \lambda^0Na^+ + \lambda^0H^+ + \lambda^0Cl^- - \lambda^0Na^+ - \lambda^0Cl^-$

$= \lambda^0CH_3COO^- + \lambda^0H^+ = \Lambda^0CH_3COOH$

10. We can construct innumerable number of Galvanic cells on the pattern of Daniel cell by taking combination of different half cells.

a) What is a Galvanic cell? (1)

b) Name the anode and cathode used in the Daniel cell? (1)

c) Name the cell represented by $Pt_{(s)}/H_{2(g)}/H^+_{(aq)}$. (½)

d) According to the convention, what is the potential of the above cell at all temperatures? (1)

e) Write the use of the above cell? (½) *[SAY 2013 & 2012]*

Ans: a) It is a device that converts chemical energy of some redox reactions to electrical energy.

b) Anode: Zn rod dipped in $ZnSO_4$ solution Or, $Zn/ZnSO_4$

Cathode: Cu rod dipped in $CuSO_4$ solution Or, $Cu/CuSO_4$

c) SHE (Standard Hydrogen Electrode)

d) Zero

e) For determining the std. electrode potential of an electrode.

11. a) The cell reaction in Daniel cell is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ and Nernst equation for single electrode potential for general electrode reaction $M^{n+}(aq) + ne^- \rightarrow M(s)$ is

$$E_{Mn+/M} = E^0_{Mn+/M} - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

Derive Nernst equation for Daniel cell. (3)

b) Daniel cell is a primary cell while lead storage cell is a secondary cell. Write any one difference between primary and secondary cell. (1) *[March 2014]*

Ans: a) Refer the Answer of the Question no. 7 (ii)

b) Primary cell cannot be recharged or reused. But secondary cell can be recharged and reused.

12. Fuel cells are special types of Galvanic cells.

a) i) What are galvanic cells? (1)

ii) Write any two advantages of fuel cells. (1)

b) Write the electrode reactions in $H_2 - O_2$ fuel cell. (2) *[SAY 2014]*

Ans: a) (i) These are devices that convert chemical energy of some redox reactions to electrical energy.

ii) *The advantages of fuel cells are:*

- *It has higher efficiency as compared to other conventional cells.*
- *It is eco-friendly since water is the only product formed.*

b) Refer the Answer of the Question no. 1 (c)

13. You are supplied with the following substances: Copper rod, zinc rod, salt bridge, two glass beakers, a piece of wire, 1 M $CuSO_4$ solution, 1 M $ZnSO_4$ solution.

a) Represent the cell made using the above materials. (1)

b) i) Write the Nernst equation for the above cell. (2)

ii) Calculate the standard emf of the cell if $E^0(Zn^{2+}/Zn) = {}^- 0.76$ V and $E^0(Cu^{2+}/Cu) = {}^+ 0.34$V (1)

[March 2015]

Ans: a) $Zn/Zn^{2+}//Cu/Cu^{2+}$(Daniel cell)

b) i) $E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$

ii) $E^0_{cell} = E^0_R - E^0_L = 0.34 - (-0.76) = 1.1$ V

14.a) Conductance (G), conductivity (K) and molar conductivity (m) are terms used in electrolytic conduction.

i) Write any two factors on which conductivity depends on. (1)

ii) How do conductivity and molar conductivity vary with concentration of electrolytic solution? (2)

b) Write any one difference between primary cell and secondary cell. (1) *[SAY 2015]*

Ans: a) (i) Conductivity depends on the nature of electrolyte and temperature.

(ii) Refer the Answer of the Question no. 5 (d)

b) Primary cell cannot be recharged or reused. But secondary cell can be recharged and reused.

15. a) Which of the following is a secondary cell?

(a) Dry cell (b) Leclanche cell (c) Mercury cell (d) None of these (1)

(b) What is the relationship between resistance and conductance? (1)

(c) One of the fuel cells uses the reaction of hydrogen and oxygen to form water. Write down the cell reaction taking place in the anode and cathode of that fuel cell. (2) *[March 2016]*

Ans: a) None of these

b) Resistance (R) = 1/Conductance (G)

c) Refer the Answer of the Question no. 1 (c)

16. Galvanic cells are classified into primary and secondary cells.

a) Write any two differences between primary and secondary cells. (2)

b) (i) What is a fuel cell? (1)

(ii) Write the overall cell reaction in $H_2 - O_2$ fuel cell? (1) *[SAY 2016]*

Ans: a) Refer the Answer of the Question no. 6 (a)

b) Refer the Answer of the Question no. 6 (b) and (c)

17. a) Represent the galvanic cell based on the cell reaction given below:

$Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$ (1)

b) Write the half cell reactions of the above cell. (1)

c) Λ^0_m for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ^0_m for HAc. (2) *[March 2017]*

Ans: (a) $Cu/Cu^{2+}//Ag^+/Ag$

(b) Anode reaction: $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode reaction: $Ag^+ + e^- \longrightarrow Ag$

(c) Refer the Answer of Question no. 1 (c)

18. a) Identify the weak electrolyte from the following:

i) KCl ii) NaCl iii) KBr iv) CH_3COOH (1)

b) Kohlrausch's law helps to determine the degree of dissociation of weak electrolyte at a given concentration.

i) State Kohlrausch's law. (1)

ii) The molar conductivity (Λ_m) of 0.001 M acetic acid is 4.95 x 10^{-5} S cm^2 mol^{-1}. Calculate the degree of dissociation (α) at this concentration if the limiting molar conductivity (λ^0_m) for H^+ is 340 x 10^{-5} S cm^2 mol^{-1} and for CH_3COO^- is 50.5 x 10^{-5} Scm^2 mol^{-1}. (2) *[SAY 2017]*

Ans: a) CH_3COOH

b) (i) Kohlrausch's law states that the limiting molar conductivity of an electrolyte is the sum of the individual contributions of the anion and the cation of the electrolyte.

(ii) $\Lambda^0_m (CH_3COOH) = \lambda^0(CH_3COO^-) + \lambda^0(H^+)$

$= 50.5 \times 10^{-5} + 340 \times 10^{-5} = 390.5 \times 10^{-5}$ Scm^2 mol^{-1}

Degree of dissociation (α) = $\lambda^c_m/\lambda^0_m = 4.95 \times 10^{-5}/(390.5 \times 10^{-5}) =$ 0.0127

19. Write the anode and cathode reactions occur in the operation of a lead storage battery. Mention the electrolyte used in the battery. (2)

Ans: Anode reaction: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode reaction: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Electrolyte used is 38% H_2SO_4.

20. a) What are primary batteries? (1)

b) The cell potential of a mercury cell is 1.35 V, and remains constant during its life. Give reason. (1)

c) Write the equations of the reactions involved at each electrode in a $H_2 - O_2$ fuel cell. (2) *[March 2018]*

Ans: (a) These are batteries which cannot be recharged or reused. Or, here the reaction occurs only once.

(b) Since the overall reaction does not involve any ion in solution.

(c) Refer the Answer of Question no. 1 (c)

21. A solution of $CuSO_4$, is electrolysed for20 minutes with a current of 1.5 amperes. What is the mass of copper deposited at cathode? (Atomic mass of copper = 63) (3)

Ans: Quantity of electricity (Q) = Current in Ampere (I) x time in second (t)

= 1.5 x 20 x 60 = 1800 Coloumb

According to the reaction; $Cu^{2+} + 2e^- \rightarrow Cu$

2F (2 x 96500 C) of electricity can deposit 1 mol of Cu = 63g Cu.

So the mass of Cu deposited by 1800 C = 63 x 1800/(2x96500) = 0.5875 g

OR

m = Zit (Where Z is the electrochemical equivalence = Equivalent wt./96500)

Here I = 1.5 A and t = 20 min. = 20 x 60 s

Equivalent wt. of Cu = Atomic mass/ valency = 63/2 = 31.5

So Z = 31.5/96500

Mass of Cu deposited = 31.5 x 1.5 x 20 x 60/96500 = 0.5875 g

22. Predict the products of electrolysis of the following substances at anode and cathode using suitable chemical equations.

(a) Aqueous NaCl (b) H_2SO_4 solution (4)

Ans: a) When aqueous NaCl is electrolysed, we get H_2 gas at the cathode and Cl_2 gas at the anode.

NaCl solution contains 4 ions – Na^+, Cl^-, H^+ and OH^-

Cathode reaction: $H^+ + e^- \rightarrow ½ H_2$

Anode reaction: $Cl^- \rightarrow ½ Cl_2 + e^-$

NaOH is formed in the solution.

b) H_2SO_4 solution contains H^+, OH^- and SO_4^{2-} ions. On electrolysis, the following reactions occur at the electrodes.

Cathode reaction: $H^+ + e^- \rightarrow ½ H_2$

Anode reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (for concentrated solution)

$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ (for dilute solution)

(peroxodisulphate ion)

23. a) Symbolically represent standard hydrogen electrode, when it acts as an anode and as cathode.

(b) Write Nernst equation for a Daniel cell. (Assume activity of metals is unity). (4) *[SAY 2018]*

Ans: a) SHE can be represented as $Pt(s)/H_2(g)/H^+(aq)$ when it acts as anode and as $H^+(aq)/H_2(g)/Pt(s)$ when it acts as cathode.

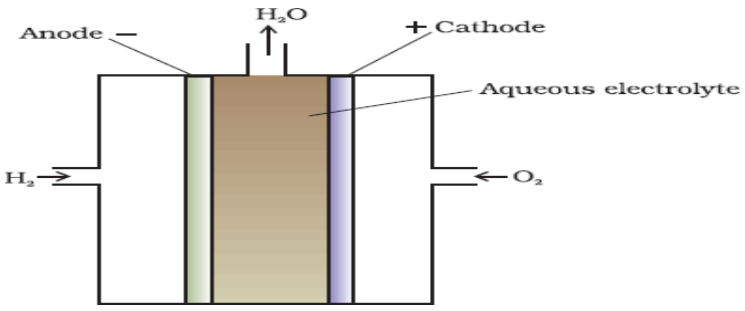
b) For a Daniel cell, the cell reaction is: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$.

The Nernst equation is: $E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$

OR, $E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

24. Diagrammatically represent $H_2 – O_2$ fuel cell and write the half cell reactions taking place in this cell. (4) *[March 2019]*

Ans:



The half cell reactions are:

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

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

[Overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$]

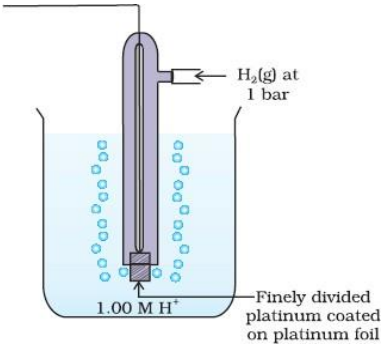
25. How do galvanic cells differ from electrolytic cells? (2)

Ans: Galvanic cells (Electrochemical cells) convert chemical energy to electrical energy while electrolytic cells convert electrical energy to chemical energy.

26. (a) Describe about standard Hydrogen Electrode (SHE). (3)

(b) The emf of the cell obtained by coupling an electrode with SHE was 1.37V. If SHE is the +ve electrode, find the potential of the given electrode. (1) *[SAY 2019]*

Ans: a) SHE consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution of one molar concentration and pure hydrogen gas at 1 bar pressure and 298K is bubbled through it. It is represented as $Pt(s)/H_2(g)/H^+(aq)$.
By convention, the electrode potential of SHE is taken as zero.
To determine the electrode potential of an electrode, it is connected in series with the standard hydrogen electrode and the emf of the resulting cell is determined by the equation, $E^0_{cell} = E^0_R - E^0_L$



b) Since SHE is the positive electrode (cathode), it is placed at the RHS.
We know that $E^0_{cell} = E^0_R - E^0_L$
i.e. $1.37 = 0 - E_L$
So, $E^0_L = -1.37V$
So the std. electrode potential of the given electrode = -1.37V

27. The limiting molar conductivity of weak electrolytes can be calculated by using the law:
a) Faraday's law b) Kohlrausch law c)Henry's law d) Raoult's law (1)
Ans: a) Kohlrausch law

28. Daniel cell converts the chemical energy liberated during the redox reaction to electrical energy.
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$; $E^0cell = 1.1$ V
(a) Identify the anode and cathode in Daniel cell (1)
(b) Calculate the standard Gibbs energy (Δ_rG^0) for the reaction. (2)
(c) Give the Nernst equation of above cell reaction. (1) *[March 2020]*

Ans: a) Anode: Zn rod dipped in $ZnSO_4$ solution Or, $Zn/ZnSO_4$
Cathode: Cu rod dipped in $CuSO_4$ solution Or, $Cu/CuSO_4$
b) $\Delta_rG^0 = -nFE^0_{cell}$
Here n = 2, F= 96500 C and $E^0cell = 1.1$ V
So $\Delta_rG^0 = -2 \times 96500 \times 1.1 = -212300$ J/mol $= -212.3$ kJ/mol
c) $E_{cell} = E^0_{cell} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$
OR, $E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

29. The cell potential of mercury cell is nearly _____.
(a) 1.50 V (b) 1.35 V (c) 1.91 V (d) 1.2 V (1)
Ans: 1.35 V

30. The rusting of iron can be considered as due to the formation of electrochemical cell on its surface.

(a) Write the anodic and cathodic reactions taking place during rusting. (2)

(b) Mention any two methods to prevent corrosion of iron. (1)

(c) Represent the galvanic cell based on the cell reaction given below:

$Cu(s) + 2Ag^+(aq) \longrightarrow Cu(aq) + 2Ag(s)$ (1) *[SAY 2020]*

Ans: (a) Anode reaction: $2\,Fe(s) \rightarrow 2\,Fe^{2+} + 4\,e^-$

Cathode reaction: $O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$

(b) The methods to prevent corrosion of metals are:

a) By giving a non-metallic coating on the metal surface with paint, varnish etc.

b) By coating the metal surface with electropositive metal like zinc, magnesium etc.

c) By coating with anti-rust solution.

d) By connecting the metal with a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the iron object (sacrificial protection). ***[Any 2 methods required]***

(c) $Cu|Cu^{2+}||Ag^+|Ag$

31. (i) The electrolyte used in Lead-storage battery is …… (1)

(ii) Give one example for a primary cell. (1)

Ans: (i) 38% H_2SO_4

(ii) Dry cell or Mercury cell

32. (i) Daniel cell is represented as $Zn(s)/Zn^{2+}(aq)//Cu^{2+}(aq)/Cu(s)$. Write Nernst equation for Daniel cell. (1)

(ii) The conductivity of 0.2M solution of KCl at 298 K is 0.024g S cm^{-1}. Calculate its molar conductivity. (2)

Ans: (i) $E_{cell} = E^0_{cell} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

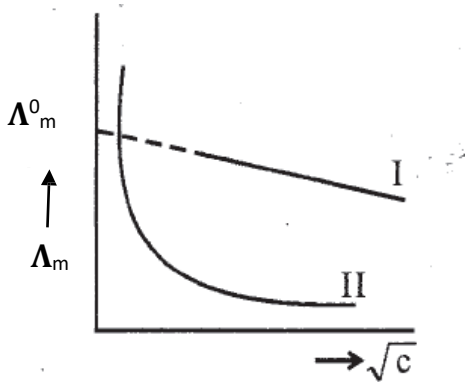
OR, $E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

(ii) Conductivity and molar conductivity are related as: $\lambda_m = 1000\,fi/M$

Here $fi = 0.0248$ S cm^{-1} and molarity, $M = 0.2$ M

*So $\lambda_m = 1000 \times 0.0248/0.2 =$ **124 S cm^2 mol^{-1}***

33. Variation of molar conductivity (Λ_m) versus concentration ($\sqrt{c}$) for a strong and weak electrolytes are given below :



(i) Identify I and II as strong and weak electrolytes. (1)

(ii) What does Λ^0_m indicate? (1)

(iii) Suggest a method to determine Λ^0_m for the electrolyte II. (1)

Ans: (i) I is strong electrolyte and II is weak electrolyte.

*(ii) $\lambda^0 m$ indicates the limiting molar conductivity **or** molar conductivity at zero concentration.*

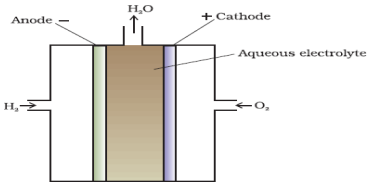
(iii) By using Kohlrausch's law

34. (i) Explain the construction and working of $H_2 - O_2$ fuel cell. (3)

(ii) Write two methods to prevent corrosion of metals. (1) *[March 2021]*

Ans: (i) In $H_2 - O_2$ fuel cells, hydrogen and oxygen gases are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are filled in the electrodes.

The electrode reactions are:
Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$
Overall reaction is: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$



(ii) Refer the Answer of Question no.29 (b)

35. Point out the advantages of fuel cells over other galvanic cells. (2)

Refer the Answer of Question no. 1 (d)

36. A galvanic cell is represented as $Mg(s)|Mg^{2+}(aq)||Ag^+(aq)|Ag(s)$

Identify the anode and cathode of the above cell and write Nernst equation for its cell potential. (3)

Ans: Anode is Mg electrode and cathode is Ag electrode

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{2F} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$OR,\ E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

37. Λ^0_m of acetic acid can be calculated, if we know the Λ^0_m values of certain suitable strong electrolytes. Explain how. (3)

Ans: Refer the Answer of Question no. 8 (iii)

38. (i) What is corrosion? (1)

(ii) Briefly explain the electrochemical processes involved in the rusting of iron. (3) *[SAY 2021]*

Ans: It is the process of formation of oxide or other compounds of a metal on its surface by the action of air, water-vapour, CO_2 etc.

(ii) Rusting of Iron is a redox reaction. At a particular spot of the metal, oxidation takes place and that spot behaves as anode. Here Fe is oxidized to Fe^{2+}. $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+. This spot behaves as cathode. The reaction taking place at this spot is:

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$$

The overall reaction is:

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

The ferrous ions (Fe^{2+}) are further oxidised to ferric ions (Fe^{3+}) and finally to hydrated ferric oxide ($Fe_2O_3.xH_2O$), which is called rust.

39. The law that can be used to determine the limiting molar conductivity (λ_m) of weak electrolytes is _____. (1)

Ans: Kohlrausch law

40. The galvanic cells which are used to convert the energy of combustion of fuels like hydrogen, methane etc into electrical energy are generally called as _____. (1)

Ans: Fuel cells

41. (i) What are secondary batteries? (1)

(ii) Write the electrode reactions and the overall cell reaction happening in the lead storage battery when it is in use. (3) *[March 2022]*

Ans: (i) Secondary cells are electrochemical cells which can be recharged and reused.

(ii) Anode reaction: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode reaction: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Net Reaction: $Pb + PbO_2 + 2\ H_2SO_4 \longrightarrow 2\ PbSO_4 + 2\ H_2O$

42. State Kohlrausch's law of independent migration of ions. (1)

Ans: Refer the Answer of Question no. 17 b (i)

43. Charge of one mole of electrons is:

(i) 1.6021×10^{-19} C (ii) 96500 C (iii) 6.022×10^{23} C (iv) 1 C (1)

Ans: (ii) 96500 C

44. (i) The standard electrode potential for Daniel cell is 1.1 V. Calculate the standard Gibbs Energy change for the reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$. (2)

(ii) Explain the working of $H_2 - O_2$ fuel cell. (2) *[SAY 2022]*

Ans: (i) We know that $\Delta G^0 = - nFE^0_{cell}$

Given $E^0_{cell} = 1.1$ V and $n = 2$

*So, $\Delta G^0 = -2 \times 96500 \times 1.1 = -212300$ J/mol = **212.3 kJ/mol***

(ii) Refer the Answer of Question no. 1 (c)

45. Λ^0_m for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S $cm^2\ mol^{-1}$ respectively. Calculate Λ^0_m for HAc. (2)

Ans: Given Λ^0m (NaCl) = 126.4 Scm^2mol^{-1}, Λ^0m (HCl) = 425.9 Scm^2mol^{-1} and Λ^0m (NaAc) = 91.0 Scm^2mol^{-1}

Applying Kohlrausch's law, $\Lambda^0m(HAc) = \Lambda^0m(NaAc) + \Lambda^0m(HCl) - \Lambda^0m(NaCl)$

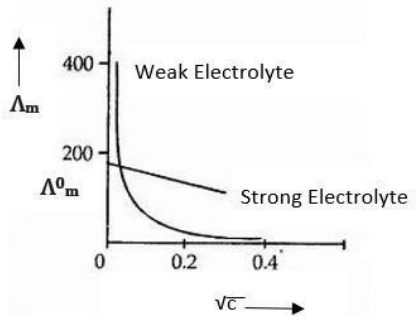
$= 91.0 + 425.9 - 126.4 = \underline{390.5\ Scm^2mol^{-1}}$

46. (i) Define Molar Conductivity. (1)

(ii) Graphically represent the variation of molar conductivity with concentration for strong and weak electrolytes. (2)

Ans: (i) Molar conductivity is the conductivity of 1 mole of an electrolytic solution kept between two electrodes of a conductivity cell with unit area of cross section and at a distance of unit length.

(ii)



47. Lead storage battery which is commonly used in automobiles is an example fora secondary cell.

(i) Write the name of anode and cathode used in this cell. (1)

(ii) Write the reactions taking place in the anode and cathode of this cell. (2)

(iii) Explain how this cell can be recharged. (1) *[March 2023]*

Ans: (i) *Anode: Lead (Pb) Cathode: A grid of lead packed with PbO_2*

(ii) Anode reaction: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode reaction: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$.

(iii) The cell can be recharged by applying an external potential higher than the potential of the cell.

48. Differentiate between primary and secondary cells. Give an example for each. (2)

Ans: Refer the Answer of Question no. 7 (a)

49. (i) How can we determine the Molar conductance at infinite dilution of acetic acid? (1)

(ii) State the Law behind this. (2)

Ans: (i) By using Kohlrausch's law OR, Refer the Answer of Question no. 9 (iii)

(ii) Kohlrausch's law states that the limiting molar conductivity of an electrolyte is the sum of the individual contributions of the anion and the cation of the electrolyte.

50. (i) Give the cell representation of Daniel cell. (1)

(ii) The standard electrode potential for Daniel cell is 1.1 V. Calculate the standard Gibb's energy change for the reaction. (2)

Ans: (i) *$Zn|Zn^{2+}||Cu^{2+}|Cu$*

(ii) $\Delta_r G^0 = -nFE^0_{cell}$

Here n = 2, F= 96500 C and E^0cell = 1.1 V

So $\Delta_r G^0 = -2 \times 96500 \times 1.1 = -212300$ J/mol = – 212.3 kJ/mol

51. (i) Write the cathode and anode reactions of $H_2 - O_2$ fuel cell. (2)

(ii) What are the advantages of fuel cells over other cells ? (2) *[SAY 2023]*

Ans: Refer the Answer of Question no. 2 (c) and (d)

##

CHEMICAL KINETICS

1. An archeological substance contained wood had only 66.66% of the ^{14}C found in a tree. Calculate the age of the sample if the half-life of ^{14}C is 5730 years. (3) *[March 2008]*

Ans: We know that radioactive decay follows first order kinetics.

For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

Here $t_{½} = 5730$ *years,* $[R]_0 = 100$ *and* $[R] = 66.66$

$k = 0.693/t_{½} = 0.693/5730 = 1.21 \times 10^{-4}$

Age of the sample, $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$$t = \frac{2.303}{1.21\ x\ 10^{-4}} \log \frac{100}{66.66}$$

$$= \underline{\mathbf{3352.38\ years}}$$

2. Unit of rate constant (k) of a reaction depends on the order of the reaction. If concentration is expressed in mol L^{-1} and time in seconds (s), find the unit of k for zero, first and second order reaction. (3) *[March 2009]*

Ans:

Reaction	*Unit of rate constant*
Zero order reaction	*mol $L^{-1}s^{-1}$*
First order reaction	*s^{-1}*
Second order reaction	*$mol^{-1}L\ s^{-1}$*

3. The order of a reaction can be zero and even a fraction but Molecularity cannot be zero or a non-integer.

i) What do you mean by the order of a reaction? (1)

ii) What is Molecularity of a reaction? (1)

iii) The conversion of molecules A to B follows second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B? (2) *[March 2010]*

Ans: i) Order of a reaction is the sum of the powers of the concentration terms of the reactants in the rate law.

ii) Molecularity of a reaction is the total number of reacting species collides simultaneously in a chemical reaction.

iii) Let the initial concentration of A be x. Then the rate law for this reaction is $r = k[x]^2$

When the concentration of A is increased to three times, the final concentration becomes 3x.

Now the rate law is $r_1 = k[3x]^2 = 9.k[x]^2$

So $r_1 = 9\ x\ r$

i.e. the rate formation of B is increased by 9 times.

4. The value of rate constant k of a reaction depends on temperature. From the values of k at two different temperatures, the Arrhenius parameters E_a and A can be calculated.

The rate constants of a reaction at 1000K and 1060K are $0.01M^{-1}\ s^{-1}$ and $0.10M^{-1}\ s^{-1}$ respectively. Find the values of E_a and A. (3) *[March 2010]*

Ans: We know that,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R} \frac{T_2 - T_1}{T_1\ T_2}$$

Here T_1 = 1000 K, k_1 = 0.01$M^{-1}S^{-1}$, T_2 = 1060 K, k_2 = 0.1 M^{-1} s^{-1} and R = 8.314 J K^{-1} mol^{-1}

$$\log \frac{0.1}{0.01} = \frac{E_a}{2.303 \times 8.314} \frac{1060 - 1000}{1000 \times 1060}$$

$$E_a = \frac{\log 10 \times 2.303 \times 8.314 \times 1000 \times 1060}{60} = 338266\ J\ mol^{-1} = \mathbf{338.266\ kJ\ mol^{-1}}$$

Also, from Arrhenius equation, $k = A.e^{\frac{-E_a}{RT}}$

$$A = \frac{k}{e^{\frac{-E_a}{RT}}} = \frac{0.01}{e^{\frac{-338266}{2.303 \times 8.314 \times 1000}}} = \mathbf{4.67 \times 10^{15}}$$

OR,

From logarithmic form of Arrhenius equation, $\log k = \log A - \frac{E_a}{2.303\ RT}$

$\log A = \log k + \frac{E_a}{2.303\ RT}$

$= \log (0.01) + \frac{338266}{2.303 \times 8.314 \times 1000} = 15.67$

A = Anti-log (15.67)

$= \mathbf{4.67 \times 10^{15}}$

5. The hydrolysis of an ester in acidic medium is a first order reaction.
   a) What do you mean by a first order reaction? (½)
   b) What is the relation between Rate constant and half-life period of a first order reaction? (½)
   c) Half-life period of a first order reaction is 20 seconds. How much time will it take to complete 90% of the reaction? (3) *[March 2011]*

Ans: a) Order of the reaction = 1. OR, it is a reaction in which rate of the reaction is directly proportional to the concentration of the reactant. i.e. r = k[R].

b) $t_{\frac{1}{2}} = \frac{0.693}{k}$

c) Here t½ = 20 s.

So k = 0.693/20 = 0.03465 s^{-1}

For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]0}{[R]}$

Let $[R]_0$ = 100. Then [R] = 100 – 90 = 10

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

$= \frac{2.303}{0.03465} \log \frac{100}{10}$

$= \mathbf{66.46\ s}$

6. The value of rate constant k of a reaction depends on temperature. From the values of k at two different temperatures, the Arrhenius parameters E_a and A can be calculated.
   a) The rate constants of a reaction at 600K and 900K are 0.02s^{-1} and 0.06s^{-1} respectively. Find the values of E_a and A. (3)
   b) Write the unit of rate constant of a 2nd order reaction if concentration is in mol L^{-1} and time in second. (1) *[SAY 2011]*

Ans: a) We know that, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R} \frac{T_2 - T_1}{T_1\ T_2}$

Here $T_1 = 600\ K$, $k_1 = 0.02\ s^{-1}$, $T_2 = 900\ K$, $k_2 = 0.06\ s^{-1}$ *and* $R = 8.314\ J\ K^{-1}\ mol^{-1}$

$$\log \frac{0.06}{0.02} = \frac{E_a}{2.303 \times 8.314} \frac{900-600}{600 \times 900}$$

$$E_a = \frac{0.4771 \times 2.303 \times 8.314 \times 600 \times 900}{300} = 16443\ J\ mol^{-1} = \mathbf{16.443\ kJ\ mol^{-1}}$$

From logarithmic form of Arrhenius equation, $\log k = \log A - \frac{Ea}{2.303\ RT}$

So, $\log A = \log k + \frac{Ea}{2.303\ RT}$

$$= \log (0.02) + \frac{16443}{2.303 \times 8.314 \times 600} = -0.267$$

A = Anti-log (- 0.267) = **0.54**

b) $Mol^{-1}L\ s^{-1}$

7. Rate of a reaction is the change in concentration of any one of the reactants or any one of the products in unit time.

i) Express the rate of the following reaction in terms of reactants and products: $2HI \rightarrow H_2 + I_2$ (1½)

ii) If the rate expression for the above reaction is rate = $k[HI]^2$, what is the order of the reaction ? (½)

iii) Define order of a reaction. (1)

iv) Whether the Molecularity and order of the above reaction are the same? Give reason (1)

[March 2012]

Ans:

i) $$r_{inst} = -\frac{1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$$

$$OR,\ r_{av} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

ii) *Order = 2*

iii) *It is the sum of the powers of the concentration terms of the reactants in the rate law.*

iv) *Yes. Here the power of the concentration term in the rate law = 2, so order =2 . The no. of reactant species = 2. So the molecularity = 2.*

8. For a first order reaction half-life period is independent of initial concentration of its reacting species.

i) What is mean by half-life period of a reaction? (1)

ii) By deriving the equation for $t_{½}$ of first order reaction, prove that $t_{½}$ is independent initial concentration of reacting species. (3) *[SAY 2012]*

Ans: i) It is the time taken to reduce the concentration of reactants to half of its initial concentration.

ii) *For a first order reaction,* $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

When $t = t_{\frac{1}{2}}$, $[R] = \frac{[R]_0}{2}$

Substitute these values in the above equation:

$$k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{[R]_0}{\frac{[R]_0}{2}}$$

$$Or,\ t_{\frac{1}{2}} = \frac{2.303 \times \log 2}{k} = \frac{2.303 \times 0.3010}{k}$$

$$Or,\ t_{\frac{1}{2}} = \frac{0.693}{k}$$

Thus for a first order reaction, half-life period is independent of initial concentration of the reacting species.

9. a) Zero order reaction means that the rate of a reaction is independent of the concentration of the reactants.
   i) Write an example for a zero order reaction. (1)
   ii) Write the integral rate expression for the zero order reaction, R → P. (1)

   b) The temperature dependence of rate of a chemical reaction can be accurately explained by Arrhenius equation. With the help of Arrhenius equation, calculate the rate constant for the first order reaction $C_2H_5I \rightarrow C_2H_4 + HI$ at 700K. Energy of activation (E_a) for the reaction is 209 kJ/mol and rate constant at 600 K is $1.6 \times 10^{-5}\ s^{-1}$ (R = 8.314 J/K/mol). (2) *[March 2013]*

Ans: a) i) Decomposition of ammonia at the surface of pt metal at high pressure.

ii) $k = \frac{[R]_0 - [R]}{t}$

b) We know that, $\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \frac{T2 - T1}{T_1\ T_2}$

Here $T_1 = 600\ K$, $k_1 = 1.6 \times 10^{-5}\ s^{-1}$, $T_2 = 700\ K$, $E_a = 209\ kJ/mol = 209 \times 10^3\ J/mol = 209000\ J\ mol^{-1}$ *and* $R = 8.314\ J\ K^{-1}\ mol^{-1}$

$$\log \frac{k_2}{1.6 \times 10^{-5}} = \frac{209000}{2.303 \times 8.314} \frac{700 - 600}{600 \times 700}$$

$$= 2.6$$

i.e. $\log k_2 - \log(1.6 \times 10^{-5}) = 2.6$

$\log k_2 = 2.6 + \log(1.6 \times 10^{-5})$

$= -2.195$

So, $k_2 = Anti\ log(-2.195) =$ ***$6.38 \times 10^{-3}\ s^{-1}$***

10. The conversion of a molecule A to B follows second order kinetics.
    a) Write the rate equation for the second order reaction. (1)
    b) If the concentration of A is increased to four times, how will it affect the formation of B. (2)
    c) Indicate the order and Molecularity of the reaction given below:

$C_{12}H_{22}O_{11} \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ (1) *[SAY 2013]*

Ans: a) $r = k[A]^2$

b) When the concentration is increased by 4 times, the new concentration of A = 4A

So, $r = k[4A]^2 = 16k[A]^2$

So the rate of formation of B is increased by 16 times.

c) Order = 1 and molecularity = 2 [It is a pseudo first order reaction].

11. a) Consider a general reaction $aA + bB \rightarrow cC + dD$. The rate expression for the reaction is $r = k[A]^x[b]^y$
    i) Establish the significance of (a+b) and (x+y) in terms of order and molecularity. (1)
    ii) Write any two differences between order and molecularity. (2)
    b) "Reactions with zero order are possible, but zero molecularity is not". Justify the statement. (1)

[March 2014]

Ans: a) i) (a+b) indicates molecularity and (x+y) indicates order.

ii)

	Order	*Molecularity*
1.	*It is the sum of the powers of the concentration terms in the rate law expression*	*It is the total number of reactant species collide simultaneously in a chemical reaction*
2.	*It is an experimental quantity*	*It is a theoretical quantity*
3.	*It can be zero or fractional*	*It cannot be zero or fractional*

b) Zero order reaction means the rate of the reaction is independent of the concentration of the reactants. So it is possible. But zero molecularity means there is no reactants. This is not possible.

12. a) Unit of rate constant (k) of a reaction depends on the order of the reactions. Values of 'k' of two reactions are given below. Find the order of each reaction.

i) $k = 3 \times 10^{-2}$ mol L^{-1} s^{-1}

ii) $k = 5 \times 10^{-3}$ mol^{-1} L s^{-1} (1)

b) i) Write integrated rate equation for a first order reaction. (1)

ii) Write the relation between half-life (t½) and rate constant (k) of a first order reaction. `(1)

iii) Rate constant of a reaction is 5×10^{-2} s^{-1}. Find the half-life (t½) of the reaction. (1) *[SAY 2014]*

Ans: a) i) Zero order ii) Second order

b) i) For first order reaction, the integrated rate equation is: $k = \frac{2.303}{t} log \frac{[R]_0}{[R]}$

ii) $k = \frac{0.693}{t_{\frac{1}{2}}}$

iii) Here $k = 5 \times 10^{-2}$ s^{-1}.

So $t_{\frac{1}{2}} = 0.693/(5 \times 10^{-2}) =$ ***13.86 s***

13. The terms order and molecularity are common in chemical kinetics.

a) What do you mean by order and molecularity? (2)

b) i) Write two factors influencing rate of a reaction. (1)

ii) Write Arrhenius equation. (1) *[March 2015]*

Ans: a) Refer the answer of the Question no. 3

b) i) Concentration of the reactants and temperature.

ii) Arrhenius equation is $k = A.e^{\frac{-E_a}{RT}}$

Or, $\log k = \log A - \frac{E_a}{2.303RT}$

14. Integrated rate expression for rate constant of a first order reaction R → P is given by $k = \frac{2.303}{t} log \frac{[R]_0}{[R]}$. Derive an expression for half-life period of first order reaction. (2)

i) A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 g of the reactant take to reduce 3g? (2) *[SAY 2015]*

Ans: i) Refer the answer of the Question no. 8 (ii)

ii) *For a first order reaction,* $k = \frac{2.303}{t} log \frac{[R]_0}{[R]}$

Here $k = 1.15 \times 10^{-3}$ s^{-1}, $[R]_0 = 5g$ *and* $[R] = 3g$

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

$= \frac{2.303}{1.15 \times 10^{-3}} log \frac{5}{3}$

$=$ ***440.5 s***

15. (i) The molecularity of the reaction $2NO + O_2 \rightarrow 2NO$, is: a) 5 b) 2 c) 3 d) 0 (1)

(ii) What do you mean by rate of a reaction ? (1)

(iii) What will be the effect of temperature on rate of a reaction ? (1)

(iv) A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find out the half-life of the reaction. (1) *[March 2016]*

Ans: i) 3

ii) It is the change in concentration of any one of the reactant or product in unit time.

iii) When temperature increases, rate of the reaction also increases.

iv) Here $k = 5.5 \times 10^{-14}\ s^{-1}$.

For a first order reaction, $t_{½} = 0.693/k = 0.693/(5.5 \times 10^{-14}) = 1.26 \times 10^{13}\ s$

16. Rate of a reaction is the change in concentration of any one of the reactants or products in unit time.

a) Express the rate of the following reaction in terms of reactants and products

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ (1)

b) (i) $N_2O_5(g) \rightarrow 2NO_2(g) + ½\ O_2(g)$ is a first order reaction. Find the unit of k. (1)

(ii) Calculate the time required for the completion of 90% of a first order reaction. ($k = 0.2303\ s^{-1}$)

(2) *[SAY 2016]*

Ans: a) $r_{inst} = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$

OR, $r_{av} = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t}$

b) (i) For a first order reaction, unit of $k = s^{-1}$

(ii) For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

For 90% completion, $[R]_0 = 100$ and $[R] = 100 - 90 = 10$

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

$t_{90\%} = \frac{2.303}{0.2303} \log \frac{100}{10}$

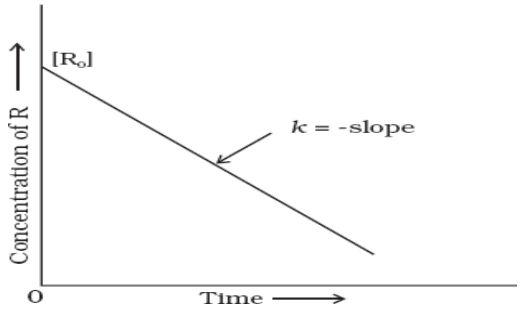
$= \mathbf{10\ s}$

17. a) Plot a graph showing variation in the concentration of reactants against time for a zero order reaction. (1)

b) What do you mean by zero order reaction? (1)

c) The initial concentration of the first order reaction, $N_2O_5(g) \rightarrow 2\ NO_2(g) + ½\ O_2(g)$, was 1.24×10^{-2} mol L^{-1} at 300 K. The concentration of N_2O_5 after 1 hour was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 300 K. (2) *[March 2017]*

Ans: (a)



(b) If the order of a reaction is zero, it is called zero order reaction. Or, these are reactions in which the rate of reaction is independent of concentration of the reactants.

(c) For a first order reaction, $k = \frac{2.303}{t} log \frac{[R]_0}{[R]}$

Here $[R]_0 = 1.24 \times 10^{-2}$ *mol/L,* $[R] = 0.2 \times 10^{-2}$ *mol/L, t = 1 hr = 60 min.*

$k = \frac{2.303}{60} log \frac{1.24 \times 10^{-2}}{0.2 \times 10^{-2}} =$ *= 0.0304* min^{-1}

18. The effect of temperature on rate of reaction is given by Arrhenius equation.
    i) Write Arrhenius equation. (1)
    ii) Define activation energy (E_a) (1)
    iii) Rate constant k_2 of a reaction at 310K is two times of its rate constant k_1 at 300 K. Calculate activation energy of the reaction. (log 2 = 0.3010 and log 1 = 0) (2) *[SAY 2017]*

Ans: i) Arrhenius equation is $k = A.e^{\frac{-E_a}{RT}}$

ii) It is the minimum amount of kinetic energy required for effective collision during a reaction.

iii) We know that, $\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \frac{T_2 - T_1}{T_1\ T_2}$

Here $T_1 = 300$ *K,* $k_1 = x$, $T_2 = 310$ *K,* $k_2 = 2x$ *and* $R = 8.314$ *J* K^{-1} mol^{-1}

$$\log \frac{2x}{x} = \frac{Ea}{2.303 \times 8.314} \frac{310 - 300}{300 \times 310}$$

$$\text{So, } E_a = \frac{2.303 \times 8.314 \times 300 \times 310 \times \log 2}{10} = \mathbf{53598\ J/mol}$$

19. Identify the order of reaction if the unit of rate constant is mol L^{-1} s^{-1}. (1)

Ans: Zero order

20. For hydrolysis of methyl acetate in aqueous solution, the following results were observed.

t/s	0	30	60
CH_3COOH C/mol L^{-1}	0.60	0.30	0.15

Show that it follows pseudo first order reaction as the concentration of water remains constant.

(3) *[March 2018]*

Ans: Here the concentration of water remains constant. So for being pseudo first order, the reaction should be first order with respect to the concentration of ester (i.e. methyl acetate). The rate constant for pseudo first order reaction is:

$k = \frac{2.303}{t} log \frac{[R]_0}{[R]}$ *where* $k = k'[H_2O]$

Here $[R]_0 = 0.6$ *mol/L.*

When t = 30 s, [R] = 0.3 mol/L

So, $k_1 = \frac{2.303}{30} log \frac{0.6}{0.3} = 0.0231\ s^{-1}$

When t = 60 s, [R] = 0.15 mol/L

So, $k_2 = \frac{2.303}{60} log \frac{0.6}{0.15} = 0.0231\ s^{-1}$

Since $k_1 = k_2$*, it is a pseudo first order reaction.*

21. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature. (3)

Ans: We know that, $\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \frac{T2 - T1}{T_1\ T_2}$

Here $T_1 = 293$ *K,* $k_1 = x$, $T_2 = 313$ *K,* $k_2 = 4x$ *and* $R = 8.314\ J\ K^{-1}\ mol^{-1}$

$\log \frac{4x}{x} = \frac{Ea}{2.303 \times 8.314} \frac{313 - 293}{293 \times 313}$

So, $Ea = \frac{2.303 \times 8.314 \times 293 \times 313 \times \log 4}{20}$ = ***52854 J/mol***

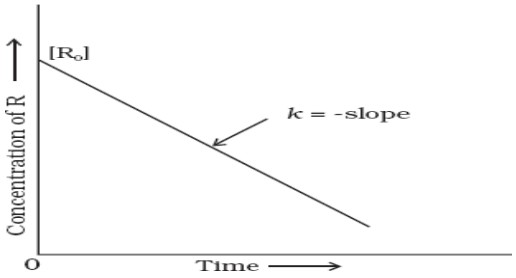
22. What is the order of a reaction, if its half-life is independent of initial concentration? (1) *[SAY 2018]*

Ans: First order.

23. For the reaction, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, the rate law is given as, Rate = $k[NO]^2\ [O_2]$. The order of the reaction with respect to O_2 is ……. (1)

Ans: With respect to O_2*, the order of the reaction = 1*

24. Examine the graph given below. Identify the integrated rate equation and the order of the reaction corresponding to it.



(2)

Ans: It's a zero order reaction.

Its integrated rate equation is $k = \frac{[R]_0 - [R]}{t}$

25. The rate constant of a reaction at 293K is $1.7 \times 10^5\ s^{-1}$. When the temperature is increased by 20 K, the rate constant is increased to $2.57 \times 10^6\ s^{-1}$. Calculate Ea and A of the reaction. (3) *[March 2019]*

Ans: We know that, $\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \frac{T2 - T1}{T_1\ T_2}$

Here $T_1 = 293K$, $k_1 = 1.7 \times 10^5 s^{-1}$, $T_2 = 293 + 20 = 313$ *K,* $k_2 = 2.57 \times 10^6\ s^{-1}$ *and* $R = 8.314\ J\ K^{-1}\ mol^{-1}$

$\log \frac{2.57 \times 10^6}{1.7 \times 10^5} = \frac{E_a}{2.303 \times 8.314} \frac{313 - 293}{293 \times 313}$

$E_a = \frac{1.179 \times 2.303 \times 8.314 \times 313 \times 293}{20}$ *= 103514 J mol*$^{-1}$ = ***103.514 kJ mol***$^{-1}$

Also, from Arrhenius equation, $k = A.e^{\frac{-E_a}{RT}}$

$A = \frac{k}{e^{\frac{-E_a}{RT}}} = \frac{1.7\ x\ 10^5}{e^{\frac{-103514}{8.314\ x\ 293}}} =$ ***4.8 x 10***^{23}

OR,

From logarithmic form of Arrhenius equation, $\log k = \log A - \frac{E_a}{2.303\ RT}$

$\log A = \log k + \frac{E_a}{2.303\ RT}$

$= \log (0.01) + \frac{103514}{2.303\ x\ 8.314\ x\ 293} = 23.68$

$A = \text{Anti-log } (23.68)$

$= \mathbf{4.8 \times 10^{23}}$

26. Differentiate molecularity and order of a reaction. (2)

Ans: Refer the answer of the Question no. 11 (a)

27. Write the Arrhenius equation and identify the terms in it. (2) *[SAY 2019]*

Ans: Arrhenius equation is $k = A.e^{-Ea/RT}$

Where k – Rate constant of the reaction, A – Arrhenius factor, Ea – Energy of activation, R – Universal gas constant and T – absolute temperature.

28. For a reaction A + B → C + D, the rate equation is $r = K [A]^{3/2}[B]^{1/2}$. Give the overall order and molecularity of the reaction. (2)

Ans: Overall Order = 2

Molecularity = 2

29. The temperature dependence of the rate of a chemical reaction can be explained by Arrhenius equation.

a) Give Arrhenius equation. (1)

b) The rate of a chemical reaction doubles for an increase of 10K in absolute temperature from 300K. Calculate the activation energy (E_a)? [R = 8.314 J/K/mol and log 2 = 0.3010] (3) *[March 2020]*

Ans: a) The Arrhenius equation is $k = A.e^{-Ea/RT}$

Or, $\log k = \log A - \frac{E_a}{2.303\ RT}$

b) We know that, $\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \frac{T2 - T1}{T_1\ T_2}$

Here $T_1 = 300K$, $T_2 = 300 + 10 = 310$ *K, and* $R = 8.314\ J\ K^{-1}\ mol^{-1}$

Suppose $k_1 = x$, *then* $k_2 = 2x$

Then,

$\log \frac{2x}{x} = \frac{Ea}{2.303 \times 8.314} \frac{310 - 300}{300 \times 310}$

$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 300 \times 310}{10}$ $= 53598.6\ J\ mol^{-1} = \mathbf{53.599\ kJ\ mol^{-1}}$

30. (a) Define molecularity. (1)

(b) Give an example of pseudo first order reaction. (1)

Ans: (a) Molecularity of a reaction is the total number of reacting species collides simultaneously in a chemical reaction.

(b) Hydrolysis of ester or inversion of cane sugar

31. (a) Write a relation which connects rate constant with temperature. (1)

(b) The rate constant for a first order reaction becomes six times when the temperature is raised from 350 K to 400 K. Calculate the activation energy for the reaction. (R = 8.314 J/K/mol) (2) *[SAY 2020]*

Ans: (a) $k = A.e^{\frac{-E_a}{RT}}$ *(The equation is known as Arrhenius equation)*

(b) We know that, $\log \frac{k2}{k_1} = \frac{Ea}{2.303\ R} \frac{T2 - T1}{T_1\ T_2}$

Here $T_1 = 350$ K, $T_2 = 400$ K, and $R = 8.314$ J K^{-1} mol^{-1}
Suppose $k_1 = x$, then $k_2 = 6x$
On substituting in the equation, we get:

$$\log \frac{6x}{x} = \frac{Ea}{2.303 \times 8.314} \frac{400 - 350}{350 \times 400}$$

$$E_a = \frac{\log 6 \times 2.303 \times 8.314 \times 350 \times 400}{50} = \underline{41715 \text{ J/mol}} = \underline{41.715 \text{ kJ mol}^{-1}}$$

32. What is a zero order reaction? Give the unit of rate constant for zero order reaction. (2)

Ans: Zero order reaction means the rate of the reaction is independent of the concentration of the reactants. Or, if the order of a reaction is zero, it is called zero order reaction. The unit of rate constant for a zero order reaction is mol L^{-1} s^{-1}.

33. The integrated rate equation for a first order reaction is:

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

(i) What is half-life period? (1)

(ii) Derive an expression for the half-life period of a first order reaction. (2)

Ans: (i) $t_{½} = \frac{0.693}{k}$

(ii) Refer the answer of question no. 8 (ii).

34. (i) Write Arrhenius equation. (1)

(ii) The rate of a reaction doubles when the temperature is increased from 298K to 308K. Calculate the activation energy. (2)

(iii) Give two differences between order and molecularity. (1) *[March 2021]*

Ans: (i) The Arrhenius equation is $k = A.e^{\frac{-E_a}{RT}}$

Or, $\log k = \log A - \frac{E_a}{2.303\ RT}$

(ii) We know that, $\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \frac{T2 - T1}{T_1\ T_2}$

Here $T_1 = 298$ K, $T_2 = 308$ K, and $R = 8.314$ J K^{-1} mol^{-1}
Suppose $k_1 = x$, then $k_2 = 2x$
Then,

$$\log \frac{2x}{x} = \frac{Ea}{2.303 \times 8.314} \frac{308 - 298}{298 \times 308}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10} = 52897.7 \text{ J mol}^{-1} = \mathbf{52.898 \text{ kJ mol}^{-1}}$$

(iii) Refer the answer of the Question no. 11 (a) ii)

35. Differentiate order and molecularity of a reaction. (2)

Ans: Refer the answer of the Question no. 11 (a) ii)

36. Derive an equation for the half-life of a first order reaction. (3)

Refer the answer of the Question no. 33 (ii)

37. Consider the pseudo order reaction, $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

(i) Identify the order and molecularity of the above reaction. (2)

(ii) Give the rate law expression of the above reaction. (1)

(iii) What happens to the rate of the above reaction when the concentration of $CH_3COOC_2H_5$ is doubled? (1)

[SAY 2021]

Ans: (i) Order = 1 and Molecularity = 2

(ii) $r = k[CH_3COOC_2H_5]$

(iii) The rate of reaction also gets doubled.

38. The unit of rate constant of a first order chemical reaction is:

(a) $mol^{-1}Ls^{-1}$ (b) s^{-1} (c) $molL^{-1}s^{-1}$ (d) $mol^{-2}L^2s^{-1}$ (1)

Ans: (b) s^{-1}

39. (i) Write Arrhenius equation. (1)

(ii) How will you obtain the value of activation energy (Ea) from a graphical plot using Arrhenius equation? (1)

Ans: (i) $k = A.e^{-Ea/RT}$

(ii) We can obtain the value of Ea by plotting a graph between log k against 1/T. From the slop of this graph we can calculate activation energy as:

Slope $= \frac{-E_a}{2.303\,R}$

So, Activation energy, E_a = – slope x 2.303 x R

40. (i) Mention any two factors which influence the rate of a chemical reaction. (1)

(ii) Derive an expression for half-life of a first order reaction from its integrated rate equation. (2) *[March 2022]*

Ans: (i) Nature of reactants, Concentration of reactants, Temperature, Pressure, Effect of catalyst and influence of radiation [Any 2 factors are required].

(ii) Refer the answer of the Question no. 33 (ii)

41. The unit of rate constant of zero order reaction is_____. (1)

Ans: mol L^{-1} S^{-1}

42. (i) Define half-life period of a reaction. (1)

(ii) How half-life period of a first order reaction is related to the rate constant of the reaction? (1)

Ans: (i) It is the time taken to reduce the concentration of reactants to half of its initial concentration.

(ii) $t_{\frac{1}{2}} = \frac{0.693}{k}$

Or, for a first order reaction, half-life period is inversely proportional to the rate constant.

43. (i) Give Arrhenius equation. Explain the terms in it. (2)

(ii) What is the significance of Arrhenius equation? (1) *[SAY 2022]*

Ans: (i) The Arrhenius equation is $k = A.e^{\frac{-E_a}{RT}}$

Or, $\log k = \log A - \frac{E_a}{2.303\,RT}$

Where k is the rate constant, A is the Arrhenius factor or pre-exponential factor, Ea is the activation energy, R is the Universal gas constant and T is the absolute temperature.

(ii) This reaction gives the temperature dependence of rate of a reaction.

44. The unit of rate constant of a zero order chemical reaction is …… (1)

Ans: mol L^{-1} s^{-1} OR, M s^{-1}

45. (i) What are pseudo first order reactions? (1)

(ii) Write one example for pseudo first order reaction. (1)

Ans: (i) These are reactions which appears to follow higher order, but actually follows first order.

(ii) Hydrolysis of ester OR, Inversion of cane sugar

46. (i) A first order reaction is found to have a rate constant, k = 6.8 x 10^{14} s. Find the half-life of the reaction. (1)

(ii) Write the integrated rate equation for a first order reaction and explain the terms in it. (2)

Ans: (i) Here k = 6.8 x 10^{-14} s^{-1}

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{6.8\ x\ 10^{-14}} = \mathbf{1.019\ x\ 10^{13}\ s}$$

(ii) Integrated rate equation for a first order reaction is:

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

Where k – rate constant, t- time taken, $[R]_0$ – Initial concentration of the reactant and [R] is the concentration of the reactant at time 't'.

47. Explain the effect of temperature and catalyst on the rate of chemical reaction. (3) [March 2023]

Ans: When temperature increases, the fraction of molecules with energy equal to or greater than activation energy increases. So, the rate of reaction also increases. A catalyst increases the rate of a reaction by providing a new path for the reaction with low activation energy.

48. Give an example for a Pseudo first order reaction. (1)

Ans: Hydrolysis of ester OR, Inversion of cane sugar

49. Calculate the half-life period of a first order reaction whose rate constant is 200 s^{-1} . (2)

Ans: Here k = 200 s^{-1}

For a first order reaction,

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{200} = \mathbf{0.0035\ s}$$

50. Write three differences between order and molecularity. (3) [SAY 2023]

Ans: Refer the Answer of the Question number 11 (a) (ii).

$$$

d and f block elements

1. Transition elements show variable oxidation states and many of the transition metal ions are attracted by a magnetic field.
   a) Give reason for variability of oxidation state. (1)
   b) Name the two types of magnetic behaviour. (1)

   Ans: a) This is because in transition elements d and s electrons have comparable energies. So along with s-electrons, d-electrons also participate in chemical reactions.
   b) Diamagnetism and paramagnetism
2. The observed magnetic moment of Sc^{3+} was found to be zero. Calculate the magnetic moment of Sc^{3+} using the spin-only formula and compare the result of observed and calculated magnetic moment. (2) *[March 2008]*

   Ans: The valence shell electronic configuration of Sc^{3+} ion is $3d^0$.
   So the number of unpaired electrons (n) = 0
   Magnetic mpment, $\mu_s = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0$.
   i.e. the observed magnetic moment is in agreement with the calculated magnetic moment.
3. A list of Lanthanide ions are given:
   La^{3+}, Ce^{4+}, Yb^{2+}, Lu^{3+}
   Atomic numbers of La, Ce, Yb and Lu are 57, 58, 70 and 71 respectively.
   a) Give the number of unpaired electrons in each ion. (1)
   b) Identify the ions which are paramagnetic. Justify. (1½)
   c) Identify the ions which are colourless. Give reason. (1½) *[SAY 2008]*

   Ans:
   a) The valence shell electronic configuration of La^{3+} ion is $4f^0$. So the number of unpaired electrons = 0.
   The valence shell electronic configuration of Ce^{4+} ion is $4f^0$. So the number of unpaired electrons = 0.
   The valence shell electronic configuration of Yb^{2+} ion is $4f^{14}$. So the number of unpaired electrons = 0.
   The valence shell electronic configuration of Lu^{3+} ion is $4f^{14}$. So the number of unpaired electrons = 0.
   b) All these ions are diamagnetic, since they contain only paired electrons.
   c) All these ions are colourless, since they do not contain any partially filled orbitals.
4. Potassium permanganate is a powerful oxidising agent in neutral, acidic and alkaline medium. In the lab, students were asked to convert an iodide to iodate. One of the students obtained I_2 instead of iodate.
   a) i) What is the reaction to be carried out by the students who got iodate? Write the chemical equation. (1½)
      ii) What may be the reaction carried out by the student who got I_2 as one of the products? (1)
   b) i) Suppose you are going the same experiment with the iodide using Potassium dichromate ($K_2Cr_2O_7$). What are the products going to be obtained? Write down the chemical equation. (1½)
      ii) What is Baeyer's reagent? (1) *[March 2009]*

   Ans: a) i) In order to get iodate, the reaction should be done in alkaline or neutral medium. The chemical equation for this reaction is: $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$
   ii) The student who got I_2 as one of the product conducted the reaction in acidic medium. The chemical equation for this reaction is: $10\ I^- + 2\ MnO_4^- + 16H^+ \rightarrow 5\ I_2 + 2\ Mn^{2+} + 8H_2O$
   b) i) The products obtained are Iodine, Cr^{3+} and water as follows:
   $6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$
   ii) Alkaline $KMnO_4$ solution is called Baeyer's reagent.
5. Potassium permanganate and Potassium dichromate are oxidising agents.
   a) Name the ores of the above compounds from which they are prepared. (½)

b) Give one example each for the oxidising property of them. Write down the balanced chemical equation. (2) *[SAY 2009]*

Ans: a) Potassium permanganate – Pyrolusite (MnO_2) and Potassium dichromate – Chromite ore ($FeCr_2O_4$)

b) Both $KMnO_4$ and $K_2Cr_2O_7$ oxidise iodides in acidic medium and liberate iodine vapours.

$$10\ I^- + 2\ MnO_4^- + 16H^+ \rightarrow 5\ I_2 + 2\ Mn^{2+} + 8H_2O$$

$$6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$$

6. Potassium permanganate is a violet crystal. What are the products obtained on strong heating of $KMnO_4$ crystals? Write the balanced chemical equation. (2) *[March 2010]*

Ans: The products obtained are Potassium manganate (K_2MnO_4), Oxygen and manganese dioxide (MnO_2).

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

7. a) Transition elements are d-block elements. Write any 4 characteristic properties of transition elements? (2)

b) Lanthanoids and actinoids are f-block elements.

i) What is the common oxidation state of Lanthanoids? (½)

ii) Name the Lanthanoid with common oxidation state +4. (½)

iii) It is difficult to separate Lanthanoids in the pure state. Explain. (1) *[SAY 2010]*

Ans: a) Transition elements are all metals, they show variable oxidation states, they form coloured compounds and most of them are paramagnetic.

b) (i) +3

(ii) Cerium (Ce)

(iii) Due to Lanthanoid contraction, lanthanoids have similar radii and hence similar physical properties. So their isolation is difficult.

8. a) Atomic size increases as we come down a group, but in 4th group of the periodic table, Zr and Hf have almost similar atomic size. Why? (1½)

b) E^0 (std. electrode potential) values generally become less negative as we move across a transition series, but E^0 values of Ni/Ni^{2+} and Zn/Zn^{2+} values are exceptions. Justify. (2½) *[March 2011]*

Ans: a) This is due to Lanthanoid contraction.

b) This is due to the highest negative hydration enthalpy of Ni^{2+} ion and completely filled d^{10} configuration of Zn^{2+} ion.

9. Transition elements are d-block elements, with some exceptions. Usually they are paramagnetic. They show variable oxidation states. They and their compounds show catalytic activity.

a) Zn (atomic number = 30) is not a transition element, though it is a d block element. Why? (1)

b) Which is more paramagnetic, Fe^{2+} or Fe^{3+}? Why? (1)

c) Why do transition elements show variable oxidation states? (1)

d) What is the reason for their catalytic property? (1) *[SAY 2011]*

Ans: a) This is due to the absence of partially filled d orbitals in the ground state or in any of the oxidation states of Zn.

b) In Fe^{3+}, there are 5 unpaired electrons. So it is more paramagnetic.

c) Due to the participation of penultimate d electrons along with valence s electrons in chemical reactions because of their comparable energies.

d) Large surface area and ability to show variable oxidation states are the reason for catalytic property.

10. a) Potassium dichromate ($K_2Cr_2O_7$) is an important compound of chromium. Describe the method of preparation of potassium chromate from chromite ore. (3)

b) The gradual decrease in the size of lanthanoid elements from lanthanum to lutetium is known as lanthanoid contraction. Write any one consequence of lanthanoid contraction. (1) *[March 2012]*

Ans: a) Potassium dichromate is generally prepared from chromite ore ($FeCr_2O_4$). The preparation involves three steps.

1. *Conversion of chromite ore to sodium chromate*

   Chromite ore is first fused with sodium carbonate in presence of air to form sodium chromate.

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

2. *Acidification of sodium chromate to sodium dichromate*

   The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodium dichromate.

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

3. *Conversion of sodium dichromate to potassium dichromate*

   The solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out.

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

b) Due to Lanthanide Contraction the 2nd and 3rd row transition series elements have similar radii.

11. Assume that you are going to present a seminar on transition elements. Prepare a seminar paper by stressing any four important properties of transition elements. (4) *[SAY 2012]*

Ans: Some important properties of transition metals are:

1. *Variable oxidation states: Transition metals show variable oxidation states. This is because in these elements d and s electrons have comparable energies. So in chemical reaction along with s-electrons, d-electrons also participate.*
2. *Magnetic properties: Transition metals show mainly two types of magnetic properties- paramagnetism and diamagnetism. Some transition metals also show ferromagnetism.*
3. *Formation of coloured compounds or ions: Most of the Transition metals ions or compounds are coloured in aqueous solution. This is because of the presence of partially filled d orbitals.*
4. *Catalytic properties: Transition metals act as catalysts in a large no. of chemical reactions. This is due to their large surface area and their ability to show variable oxidation state.*

12. Account for the following trends in atomic and ionic radii of transition elements.
    a) Ions of the same charge in a given series (3d, 4d or 5d) show progressive decrease in radii with increasing atomic number. (1)
    b) The atomic radii of elements in 4d series are more than that of corresponding elements in 3d series. (1)
    c) The atomic radii of the corresponding elements in 4d series and 5d series are virtually the same. (2) *[March 2013]*

Ans: a) This is due to the poor shielding effect and increase in nuclear charge.

b) This is due to increase in no. of shells and greater shielding effect.

c) This is due to Lanthanoid contraction.

13. d block elements belong to groups 3 – 12 in the periodic table, in which the d orbitals are progressively filled.
    a) What is their common oxidation state? (½)
    b) Name two important compounds of transition elements. (1)
    c) Transition elements form a large number of complex compounds. Why? (1½)
    d) What is misch metal? (1) *[SAY 2013]*

Ans: a) The common oxidation state is +2.

b) $K_2Cr_2O_7$ and $KMnO_4$

c) This is due to comparatively smaller size, high ionic charge, pesence of partially filled d orbitals and ability to show variable oxidation state.

d) It is an alloy of Lanthanoids which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al.

14. Potassium dichromate is an orange coloured crystal and is an important compound used as an oxidant in many reactions.

a) How do you prepare $K_2Cr_2O_7$ from chromite ore? (3)

b) How will you account for the colour of potassium dichromate crystals? (1) *[March 2014]*

Ans: a) Refer the answer of Question no. 10 (a)

b) The colour of $K_2Cr_2O_7$ is due to charge transfer spectrum.

15. Potassium permanganate and potassium dichromate are two transition metal compounds.

a) Write any four characteristics of transition metals. (2)

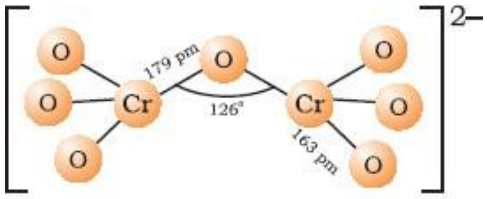
b) Write any two uses of potassium permanganate. (1)

c) Draw the structure of dichromate ion. (1) *[SAY 2014]*

Ans: a) Refer the answer of Question no. 7 (a).

b) It is used as an oxidising agent in acidic, basic and neutral medium. It is used as a primary standard in volumetric analysis.

c)



Dichromate ion

16. Fourteen elements following Lanthanum are called Lanthanoids:

a) What is Lanthanoid contraction? Give reason for it? (2)

b) $KMnO_4$ is a purple coloured crystal and it acts as an oxidant. How will you prepare $KMnO_4$ from MnO_2? (2) *[March 2015]*

Ans: a) The regular decrease in the atomic and ionic radii along lanthanide series is known as lanthanide contraction. It is due to the poor shielding effect of f – electrons and increase in nuclear charge.

b) The preparation of Potassium permanganate from Pyrolusite (MnO_2) involves two steps. In the first step MnO_2 is fused with KOH to form potassium manganate (K_2MnO_4).

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

In the second step, K_2MnO_4 is electrolytically oxidised to potassium permanganate.

$$MnO_4^{2-} \xrightarrow{\text{Electrolytic oxidation in alkaline solution}} MnO_4^-$$

17. Which of the following oxidation state is common for lanthanides?

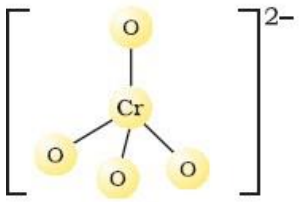
i) +2 ii) +3 iii) +4 iv) +5 (1)

b) Draw the structures of chromate and dichromate ions. (1)

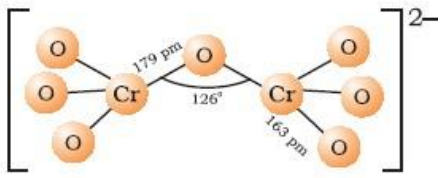
c) Zirconium (Zr) belongs to '4d' and Hafnium (Hf) belongs to '5d' transition series. It is difficult to separate them. Explain. (2) *[SAY 2015]*

Ans: a) +3

b)



Chromate ion



Dichromate ion

c) Due to lanthanoid contraction, Zr and Hf have similar radii and hence similar physical properties. So their separation is difficult.

18. a) Which of the following oxidation state is not shown by Manganese?

(i) +1 (ii) +2 (iii) +4 (iv) +7 (1)

b) Represent the structure of dichromate ion. (1)

c) Potassium permanganate ($KMnO_4$) is a strong oxidizing agent. Write oxidizing reactions of $KMnO_4$. (2)

[March 2016]

Ans: a) +1

b) Refer the answer of Question no. 15 (c)

c) In acidic medium, $KMnO_4$ oxidises ferrous salt to ferric salt.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

19. Transition elements are d-block elements and inner transition elements are f-block elements.

(i) Write any two properties of transition elements. (1)

(ii) Name a transition metal compound and write one use of it. (1)

(iii) What is Lanthanoid contraction? (1)

(iv) Write any two consequences of Lanthanoid contraction. (1) *[SAY 2016]*

Ans: (i) Refer the answer of Question no. 7 (a)

(ii) $KMnO_4$, used as an oxidising agent

(iii) It is the regular decrease in the atomic and ionic radii along lanthanide series.

(iv) Due to Lanthanide Contraction the 2^{nd} and 3^{rd} row transition series elements have similar radii. Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.

20. a) Transition elements are'd' block elements.

i) Write any four characteristic properties of transition elements. (2)

ii) Cr^{2+} and Mn^{3+} have d^4 configuration. But Cr^{2+} is reducing and Mn^{3+} is oxidising. Why? (1)

b) Which of the following is not a Lanthanoid element?

i) Cerium ii) Europium iii) Lutetium iv) Thorium (1) *[March 2017]*

Ans: a) (i) Refer the answer of Question no. 7 (a)

(ii) This is due to the extra stability of Cr^{3+} and Mn^{2+} ions.

b) Thorium

21. a) Zr and Hf are having similar chemical properties. This is due to ..... (1)

b) 'Magnetic moments arise due to the presence of unpaired electrons'.

Calculated magnetic moments of two transition metal ions are given below.

Ion	Calculated magnetic moment
Sc^{3+}	0
Ti^{3+}	1.73

Justify these observations on the basis of spin only formula. (2)

c) Transition metal ions are generally coloured. Why? (1) *[SAY 2017]*

Ans: a) Lanthanoid contraction

b) The spin only magnetic moment $\mu_s = \sqrt{n(n+2)}$, where n is the no. of unpaired electrons.

For Sc^{3+} the electronic configuration is $3d^0$. So there is no unpaired electron and hence $\mu_s = 0$.

Ti^{3+} the electronic configuration is $3d^1$. So there is one unpaired electron and hence $\mu_s = \sqrt{1(1+2)} = 1.73$ BM

c) This is due to the presence of partially filled d-orbitals or due to d-d transition.

22. What is the structure of chromate ion ((CrO_4^{2-}))? (1)

Ans: a) Tetrahedral

23. Give reasons for the following :

(a) Transition metals and many of their compounds act as catalyst. (1)

(b) Scandium (Z = 21) does not exhibit variable oxidation state and yet it is regarded as a transition element. (1)

(c) Write the steps involved in the preparation of Na_2CrO_4 from chromite ore. (1) *[March 2018]*

Ans: (a) Due to their large surface area and their ability to show variable oxidation state.

(b) Due to the presence of partially filled d-orbitals in Scandium.

(c) Chromite ore is fused with sodium carbonate in presence of air to form sodium chromate.

Or, the equation: $4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$

24. What is the magnetic moment of an atom having d^{10} configuration? (1)

Ans: zero

25. Describe lanthanoid contraction. Write any two consequences of it. (3) *[SAY 2018]*

Ans: Refer the answers of Question no. 16 (a) and 19 (iv).

26. MnO_4^- and ….. are formed by the disproportionation of MnO_4^{2-} in acidic medium. (1)

Ans: MnO_2 (Manganese dioxide)

27. Write any three applications of d- and f- block elements. (3) *[March 2019]*

Ans: d and f block elements and their compounds are used as catalysts in many chemical reactions. Iron and steels are the most important construction materials. Alloys of d and f block elements are used in various fields. Cu, Ag, Au and some alloys are used for making coins. TiO is used in pigment industry. Zn, Ni, Cd, MnO_2 etc are used in making batteries. Compounds of Ag are used in photography.

[Only 3 required]

28. Which element of the 3d series exhibits the largest number of oxidation states? Why? (2)

Ans: Manganese (Mn)

29. What is Lanthanoid contraction? Give reason for it. (2) *[SAY 2019]*

Ans: Refer the answers of Question no. 16 (a)

30. (a) In d-block elements the radii of elements of third transition series are similar to those of the elements of second transition series. Give reason. (1)

(b) Outer electronic configuration of Cu^{2+} ion is $3d^9$. Calculate its spin only magnetic moment. (1)

Ans: (a) Due to Lanthanoid contraction.

(b) For $3d^9$ configuration, there is only one unpaired electron and hence $\mu_s = \sqrt{1(1+2)} = 1.73$ BM

31. Give the steps involved in the preparation potassium dichromate ($K_2Cr_2O_7$) from chromite ore. (3) *[March 2020]*

Ans: Refer the answers of Question no. 10 (a)

32. (a) What is the common oxidation state of Lanthanoids? (1)

(b) Atomic sizes increases as we move down a group, but in 4^{th} group of the periodic table Zr and Hf have almost the same atomic sizes. Why? (1)

Ans: (a) +3

(b) Due to Lanthanoid contraction.

33. Transition elements show various oxidation states and many of the transition metal ions are attracted by a magnetic field.

(a) Give reason for variability of oxidation state. (1)

(b) Name the two types of magnetic behaviour. (1)

(c) Calculate the 'Spin only' magnetic moment of M^{2+}(aq) ion (Z = 27). (1) *[SAY 2020]*

Ans: (a) This is because in transition elements d and s electrons have comparable energies. So along with s-electrons, d-electrons also participate in chemical reactions.

(b) Diamagnetism and Paramagnetism.

(c) For M^{2+} ion with atomic number 27, the electronic configuration is $3d^7$. So there are 3 unpaired electrons and hence $\mu_s = \sqrt{3(3+2)} = 3.87$ BM

34. Potassium dichromate is a very useful oxidizing agent.
(i) Name the ore of Potassium dichromate. (1)
(ii) Explain the preparation of Potassium dichromate from Sodium chromate. (2)

Ans: (i) Chromite ore (Fe_2CrO_4)

(ii) First sodium chromate is acidified with sulphuric acid to produce sodium dichromate.

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

Then the solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out.

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

35. (i) Account for the following :
A. Zr and Hf have identical radii. (1)
B. Transition metals are very good catalysts. (1)
(ii) Calculate the spin only magnetic moment of M^{2+}(aq) ion (Z = 27). (1) *[March 2021]*

Ans: (i) A. Due to lanthanoid contraction/lanthanide contraction.

B. This is due to their large surface area and their ability to show variable oxidation state.

(ii) For M^{2+} ion with atomic number 27, the electronic configuration is $3d^7$. So there are 3 unpaired electrons and hence $\mu_s = \sqrt{3(3+2)} = \overline{3.87\ BM}$

36. Explain the steps involved in the preparation of $K_2Cr_2O_7$ from $FeCr_2O_4$. (3)

Ans: Refer the Answer of Question number 10 (a)

37. What is meant by lanthanoid contraction? Give any two of its consequences. (3) *[SAY 2021]*

Ans: Refer the Answer of Question number 19 (iii) & (iv)

38. What is lanthanoid contraction? Mention any one of its consequences. (2)

Refer the Answer of Question number 19 (iii) & (iv)

39. Why is Cr^{2+} reducing and Mn^{3+} oxidizing when both have d^4 configuration? (2) *[March 2022]*

Ans: This is due to the extra stability of Cr^{3+} and Mn^{2+} ions.

When Cr^{2+} loses one electron, its configuration becomes d^3, which is equal to the stable half filled t_{2g}^3 configuration. So Cr^{2+} readily loses electron and acts as a reducing agent.

When Mn^{3+} gains one electron, it attains the stable half filled d^5 configuration. So Mn^{3+} acts as an oxidising agent.

40. The atomic radii of Zr and Hf are almost identical. Justify. (2)

Ans: Due to lanthanoid contraction, Zr and Hf have similar radii and hence similar physical properties.

41. How can you prepare $KMnO_4$ from MnO_2? (2) *[SAY 2022]*

Ans: Refer the Answer of Question number 16 (b)

42. Among the following transition elements which one has a completely filled d orbital?
(a) Ag (b) Ti (c) Mo (d) Ni (1)

Ans: (a) Ag

43. (i) Transition elements show variable oxidation state. Why? (1)
(ii) Identify the element in the 3d transition metal series that exhibits maximum number of oxidation states. (1)

Ans: (i) Refer the Answer of Question number 9 (c)

(ii) Manganese (Mn)

44. Write the preparation of $K_2Cr_2O_7$ from Chromite ore. (3) *[March 2023]*

Refer the Answer of Question number 10 (a)

45. The oxidation number of Manganese in $KMnO_4$ is _____ (1)

Ans: +7

46. Explain Lanthanoid contraction. (2)

Refer the Answer of Question number 16 (a)

47. Mention the three steps involved in the manufacture of Potassium dichromate. (3) *[SAY 2023]*

Refer the Answer of Question number 10 (a)

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CO-ORDINATION COMPOUNDS

1) A list of co-ordination compounds are given below: $[PtCl_2(NH_3)_2]$, $[PtCl_2(NH_3)_4]Br_2$, $[Cr(H_2O)_6]Cl_3$.
Which type of isomerism do these compounds exhibit? (3) *[March 2008]*

Ans: $[PtCl_2(NH_3)_2]$ – Geometrical isomerism
$[PtCl_2(NH_3)_4]Br_2$ – Ionisation isomerism and Geometrical isomerism
$[Cr(H_2O)_6]Cl_3$ – Hydrate (Solvate) isomerism

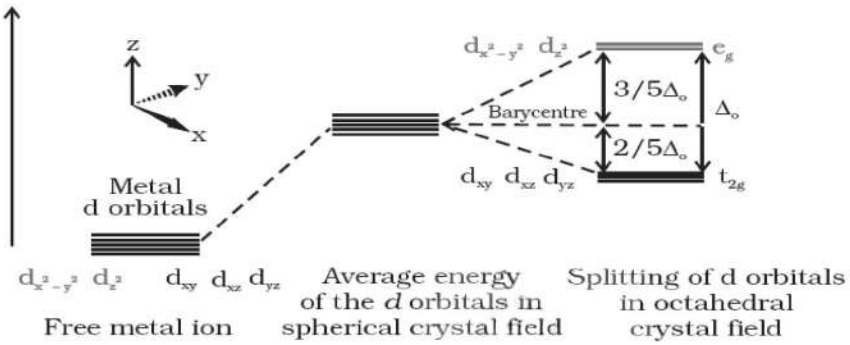
2) Teacher asked two students to write the electronic configuration of d^4 system using CFT.
Student I: $t_{2g}^3\ e_g^1$
Student II: $t_{2g}^4\ e_g^0$

a) Suggest which student gives correct configuration. Justify your answer. (2)

b) Draw figure to show splitting of degenerate d-orbitals in an octahedral crystal field. (1) *[SAY 2008]*

Ans: a) Both of the configurations are correct depending on the strength of the ligand. If the ligand is weak field, student I is correct. If the ligand is strong field, student II is correct.

b)



3) The central metal ion Co^{3+} with co-ordination number 6 can form a series of complexes in which both Cl^- and NH_3 are acting as ligands.

a) Give the formulae of each complex molecule (three molecules). (1½)

b) Give the IUPAC names of the above complexes. (1½) *[March 2009]*

Ans: a) $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$
b) $[Co(NH_3)_5Cl]Cl_2$ – Pentaamminechloridocobalt(III)chloride
$[Co(NH_3)_4Cl_2]Cl$ – Tetraamminedichloridocobalt(III)chloride
$[Co(NH_3)_3Cl_3]$ – Triamminetrichloridocobalt(III)

4) $[Cr(NH_3)_4Cl_2]Br$ is a co-ordination compound.

a) Identify the central metal ion of the above compound. (½)
b) Name the ligands present in it. (1)
c) What is its co-ordination number? (½)
d) Write the IUPAC name. (1)
e) Write the ionisation isomer of the above compound. (1) *[March 2010]*

Ans: a) Cr^{3+}
b) NH_3 and Cl^-
c) 6
d) Tetraamminedichloridochromium(III)bromide
e) $[Cr(NH_3)_4ClBr]Cl$

5) Na_2EDTA is used in the estimation of hardness of water.

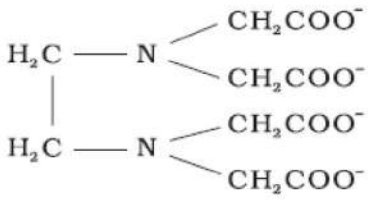
a) Draw the structure of $EDTA^{4-}$. (1)

b) What is its denticity? (½)

c) What are the donor atoms in it? (½)

d) Why is it called a chelating ligand? (1) *[March 2010]*

Ans: a)



b) Denticity = 6

c) Here the donor atoms are Oxygen and Nitrogen.

d) It can form ring complexes with the central atom. So it is a chelating ligand.

6) a) NO_2^- and ONO^- constitute ambidentate ligands. Give another set of ambidentate ligands. (1)

b) $EDTA^{4-}$ is a chelating ligand. Give two other examples. (1)

c) Give the denticity of NO_2^- and NH_3. (1) *[March 2010]*

Ans: a) SCN^- and NCS^-

b) Ethane-1,2-diamine (en) and oxalate ion ($C_2O_4^{2-}$)

c) 1

7) The central ion Ag^+ with co-ordination number 2 forms a positive complex ion with NH_3 ligand. Also Ag^+ forms a negative complex with CN^- ligand.

a) Write the formulae of the above positive and negative complex ions. Give the IUPAC name of each. (2)

b) Give the denticity of NH_3 and CN^- ligands. (1)

c) Write the formula and name of a hexadentate ligand. (1) *[SAY 2011]*

Ans: a) $[Ag(NH_3)_2]^+$ - Diamminesilver(I) and $[Ag(CN)_2]^-$ - Dicyanidoargentate(I)

b) 1

c) $EDTA^{4-}$ (Ethylenediaminetetraacetate ion)

8) Consider the co-ordination compound $[Co(NH_3)_5SO_4]Br$.

a) Write the IUPAC name of the above co-ordination compound. (1)

b) What are the primary and secondary valencies of the central metal cobalt in the above co-ordination compound? (1)

c) Which type of structural isomerism is exhibited by the above co-ordination compound? (1) *[March '12]*

Ans: a) Pentaamminesulphatocobalt(III)bromide

b) Primary valency = 3 and secondary valency = 6

c) Ionisation isomerism

9) $[Cr(NH_3)_5CO_3]Cl$ is a co-ordination compound.

a) Name the central metal ion of the above compound. (1)

b) What is the IUPAC name? (1)

c) Name the ligands present in the above compound. (1)

d) Whether the ligands present in the above compound are ambidentate ligands? Why? (1)

e) What is the ionisation isomer of the above mentioned co-ordination compound? (1) *[SAY 2012]*

Ans: a) Cr^{3+}

b) Pentaamminecarbonatochromium(III)chloride

c) NH_3 *and* CO_3^{2-}

d) Since they do not contain more than one donor atoms, they are not ambidentate ligands.

e) $[Cr(NH_3)_5Cl]CO_3$

10) The magnetic behaviour of a complex can be explained on the basis of Valence Bond (V.B) theory.

a) $[Co(NH_3)_6]^{3+}$ is a diamagnetic complex and $[CoF_6]^{3-}$ is a paramagnetic complex. Substantiate the above statement using V.B theory. (3)

b) Classify the above mentioned complexes into inner orbital and outer orbital complexes. (1)

[March 2011 & 2013]

Ans: a) In $[Co(NH_3)_6]^{3+}$*, the electrons get paired in presence of the strong field ligand* NH_3*. So there is no unpaired electron and hence it is diamagnetic. But in* $[CoF_6]^{3-}$*,* F^- *is a weak field ligand and hence electrons do not get paired. So there is unpaired electron and hence it is paramagnetic.*

b) $[Co(NH_3)_6]^{3+}$ *is an inner orbital complex, while* $[CoF_6]^{3-}$ *is an outer orbital complex.*

11) Many theories have been put forth to explain the nature of bonding in co-ordination compounds.

a) On the basis of valence bond theory account for the diamagnetic behaviour of $[Ni(CN)_4]^{2-}$. (1½)

b) What is the shape of the above complex? (½)

c) Arrange the following ligands in the increasing order of their field strengths (as in spectrochemical series). Cl^-, CO, H_2O, OH^- (1) *[SAY 2013]*

Ans: a) In $[Ni(CN)_4]^{2-}$*,* CN^- *is a strong field ligand and hence all the electrons get paired. So there is no unpaired electron and hence the complex is diamagnetic.*

b) Square planar

c) $Cl^- < OH^- < H_2O < CO$

12) $[Co(NH_3)_5SO_4]Cl$ is an octahedral co-ordination compound.

a) Write the IUPAC name of the above compound. (1)

b) Write the formula of the ionization isomer of the above compound. (1)

c) How do d - orbitals split in an octahedral crystal field? (1)

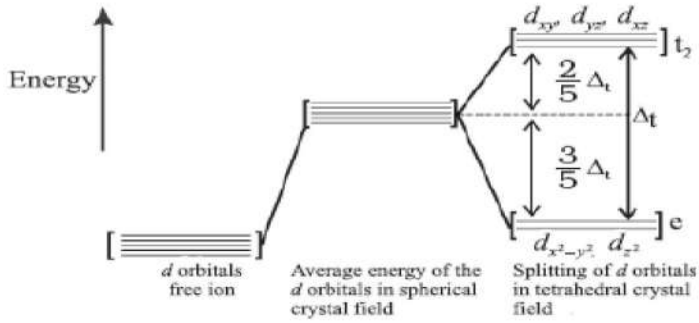
d) Draw the diagram which indicates the splitting of d-orbitals in tetrahedral field. (1) *[March 2014]*

Ans: a) Pentaamminesulphatocobalt(III)chloride

b) $[Co(NH_3)_5Cl]\ SO_4$

c) In octahedral field, d-orbitals split into two – the lower energy t_{2g} *levels and the higher energy* e_g *levels.*

d)



13) a) Valence Bond Theory (VBT) can explain the magnetic behaviour and shape of complexes. Using VBT explain the diamagnetism and square planar shape of $[Ni(CN)_4]^{2-}$. (2)

b) i) Suggest the shape of the following complexes – $[Ni(CO)_4]$ and $[CoF_6]^{3-}$ (1)

ii) The central ion Co^{3+} with co-ordination number 6 is bonded to the ligands NH_3 and Br^- to form a dipositive complex ion. Write the formula or IUPAC name of the complex ion. (1) *[SAY 2014]*

Ans: a) In $[Ni(CN)_4]^{2-}$, the central atom Ni is in dsp^2 hybridisation. So it has a square planar geometry. Due to the absence of unpaired electrons, the complex is diamagnetic.

b) i) $[Ni(CO)_4]$ is tetrahedral complex and $[CoF_6]^{3-}$ is octahedral complex.

ii) $[Co(NH_3)_5Br]^{2+}$ [Pentaamminebromidocobalt(III)]

14) Co-ordination compounds contain central metal atom/ion and ligands.

a) Primary valency of central metal atom/ion in $[Co(NH_3)_6]Cl_3$ is:

i) 3 ii) 6 iii) 4 iv) 9 (1)

b) i) What are the postulates of Werner's theory? (2)

ii) Write the IUPAC names of $K_3[Fe(CN)_6]$ and $[Co(NH_3)_6]Cl_3$. (1) *[March 2015]*

Ans: a) 3

b) i) The important postulates of Werner's theory are:

1. *Every metal has two types of valencies – primary (1^0) valency and secondary (2^0) valency. Primary valency is ionisable, while secondary valency is non-ionisable.*
2. *Primary valency is denoted by doted lines, while secondary valency is denoted by thick lines.*
3. *Primary valency gives the oxidation state of the metal, while secondary valency gives the co-ordination number of the metal.*
4. *Primary valency is always satisfied by –ve ions, while secondary valency may be satisfied by –ve ions or neutral molecules.*
5. *Every metal has a fixed number of secondary valencies. In order to satisfy this requirement, some –ve ions may perform dual character – i.e., they act as primary and secondary valencies simultaneously.*
6. *The primary valencies are non-directional, while the secondary valencies are directional. i.e. they are directed to some fixed positions in space.*
7. *Since secondary valencies are directional, co-ordination compounds have a definite geometry and they show isomerism. [Here only 2 postulates are required]*

ii) $K_3[Fe(CN)_6]$ – Potassiumhexacyanidoferrate (III) and $[Co(NH_3)_6]Cl_3$ – Hexaamminecobalt(III)chloride.

15) a) Write the IUPAC name of the complex $K_3[Cr(C_2O_4)_3]$. (1)

b) Draw the figure to show the splitting of 'd' orbitals in octahedral crystal field. (1)

c) $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic, whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Write the reason. (2) *[SAY 2015]*

Ans: a) Potassiumtrioxalatochromate (III)

b) Refer the answer of the question number 2 (b).

c) In $[Fe(H_2O)_6]^{3+}$, H_2O is a weak field ligand and so electron pairing does not occur. Hence there are 5 unpaired electrons and it is strongly paramagnetic. But in $[Fe(CN)_6]^{3-}$, electron pairing occurs in presence of the strong ligand CN^-. So there is only one unpaired electron and in weakly paramagnetic.

16) a) Write down the ionization isomer of $[Co(NH_3)_5Cl]SO_4$. (1)

b) Write the IUPAC name of the above compound. (1)

c) $[Ni(CO)_4]$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic though both are tetrahedral. Why? (2)

[March 2016]

Ans: a) $[Co(NH_3)_5SO_4]Cl$

b) Pentaamminechloridocobalt(III)sulphate

c) In $[Ni(CO)_4]$, there is no unpaired electron. So it is diamagnetic. But in $[NiCl_4]^{2-}$, there are 2 unpaired electrons. So it is paramagnetic.

17) Consider the co-ordination compound $[Co(NH_3)_5Cl]Cl_2$.

a) Write the IUPAC name of the above compound. (1)

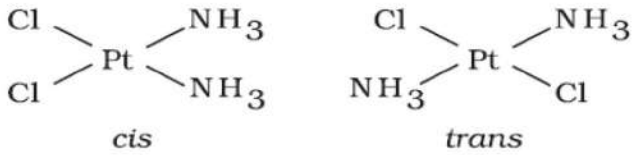
b) i) What is the primary valency and secondary valency of the central metal ion in the above co-ordination compound? (1)

ii) Write the name of isomerism exhibited by the complex $[Pt(NH_3)_2Cl_2]$. Represent the possible isomers. (2) *[SAY 2016]*

Ans: a) Pentaamminechloridocobalt(III)chloride

b) i) Primary valency = 3 and secondary valency = 6

ii) Geometrical isomerism.



18) $[Co(NH_3)_5SO_4]Cl$ and $[Co(NH_3)_5Cl]SO_4$ are co-ordination compounds.

a) Identify the isomerism shown by the above compounds. (1)

b) Write the IUPAC names of the above compounds. (2)

c) Identify the ligands in each of the above compounds. (1) *[March 2017]*

Ans: (a) Ionisation isomerism.

(b) $[Co(NH_3)_5SO_4]Cl$ – Pentaamminesulphatocobalt(III)chloride
$[Co(NH_3)_5Cl]SO_4$ – Pentaamminechloridocobalt(III)sulphate

(c) In the compound $[Co(NH_3)_5SO_4]Cl$, the ligands are NH_3 and SO_4^{2-} and in $[Co(NH_3)_5Cl]SO_4$, the ligands are NH_3 and Cl^-.

19) a) In which of the following, the central atom/ion is in zero oxidation state.

i) $[Ni(CN)_4]^{2-}$ ii) $[NiCl_4]^{2-}$ iii) $[Ni(CO)_4]$ iv) $[Ni(NH_3)_6]^{2+}$ (1)

b) $[Ni(CN)_4]^{2-}$ has square planar structure and it is diamagnetic.

i) On the basis of valence bond theory explain why $[Ni(CN)_4]^{2-}$ exhibit these properties. (2)

ii) Identify the ligand in the above mentioned complex. (1) *[SAY 2017]*

Ans: a) $[Ni(CO)_4]$

b) i) In $[Ni(CN)_4]^{2-}$, the central atom Ni is in dsp^2 hybridisation. So it has a square planar geometry. Due to the absence of unpaired electrons, the complex is diamagnetic.

c) The ligand in this complex is CN^-

20) Explain how the complexes of nickel, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ have different structures, but do not differ in their magnetic behaviour. (Atomic no. of Ni = 28) (2)

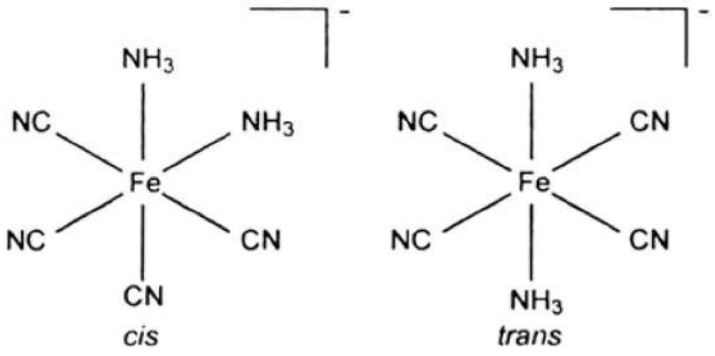
*Ans: In $[Ni(CN)_4]^{2-}$, Ni is dsp^2 hybridized and so it has **square planar geometry**. But in $[Ni(CO)_4]$, Ni is sp^3 hybridized and so it has **tetrahedral shape**. Due to the absence of unpaired electrons, both are diamagnetic.*

21) (a) Draw the structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$ (2)

(b) Write the formula of pentaamminecarbonatocobalt (III) chloride. (1)

(c) Write any two limitations of valance bond theory. (1) *[March 2018]*

Ans: (a)



(b) $[Co(NH_3)_5(CO_3)]Cl$

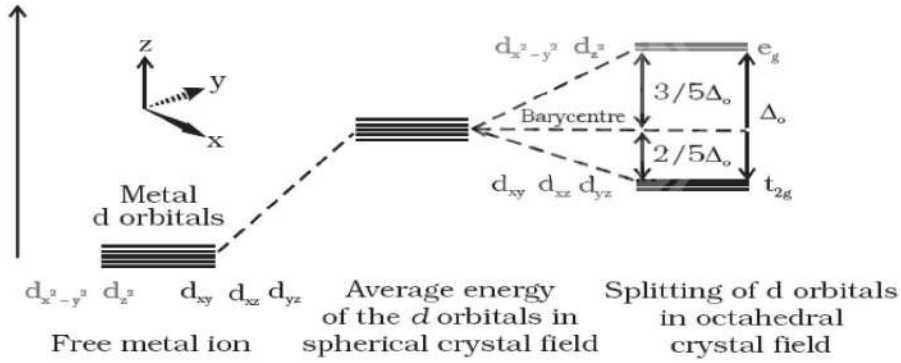
(c) Limitations of valence bond theory are:

(i) It involves a large number of assumptions.

(ii) It does not explain the colour exhibited by co-ordination compounds.

22) Draw a diagram depicting crystal field splitting in an octahedral environment of d-orbitals. Label the diagram properly. Calculate the crystal field stabilization energy for a d^3 configuration. (4) *[SAY 2018]*

Ans:



For d^3 systems, the configuration is t_{2g}^3.

The crystal field stabilization energy is -3 x 2Δo/5= - 6 x Δo/5

23) Identify the co-ordination compound which can exhibit linkage isomerism, among the following:

(a) $[Pt(NH_3)_2Cl_2]$ (b) $[Co(NH_3)_5(SO_4)]Br$ (c) $[Co(NH_3)_5(NO_2)]Cl_2$ (d) $[Cr(NH_3)_6][CoF_6]$ (1)

Ans: (c) $[Co(NH_3)_5(NO_2)]Cl_2$

24) (i) With the help of a diagram give the splitting of d-orbitals of Mn^{2+} ion in an octahedral crystal field. (2)

(ii) On the basis of crystal field theory, explain why $[Mn(H_2O)_6]^{2+}$ contains five unpaired electrons while $[Mn(CN)_6]^{4-}$ contains only one unpaired electron. (2) *[March 2019]*

Ans: (i) Refer the answer of Question no. 22

(ii) In $[Mn(H_2O)_6]^{2+}$, H_2O is a weak field ligand. Here the magnitude of Δo is less than the energy required for electron pairing. So the configuration is $t_{2g}^3e_g^2$. Hence it contains 5 unpaired electrons. But in $[Mn(CN)_6]^{4-}$, CN- is a strong field ligand and hence Δo > the pairing energy. So the configuration is t2g5. Hence it contains only one unpaired electron.

25) The crystal field splitting energy for Octahedral (Δo) and Tetrahedral (Δt) complexes are related as

(a) $\Delta t = 3/5\Delta o$ (b) $\Delta t = 5/3\Delta o$ (c) $\Delta t = 4/9\Delta o$ (d) $\Delta t = 9/4\ \Delta o$ (1)

Ans: (c) $\Delta t = 4/9\Delta o$

26) Write the IUPAC name of the following :

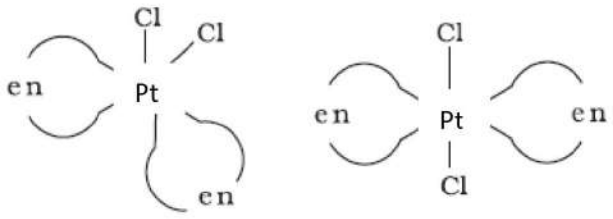
(i) $[Ni(CO)_4]$ (ii) $K_4[Fe(CN)_6]$ (2)

Ans: (i) Tetracarbonylnickel (0)

(ii) Potassiumhexacyanidoferrate (II)

27) Draw the geometrical isomers of $[PtCl_2(en)_2]^{2+}$. Which among the isomer is optically active? Give reason. (4) *[SAY 2019]*

Ans:



Cis isomer *Trans isomer*

Cis isomer is optically active, since it has no plane of symmetry. [Or, trans isomer has a plane of symmetry and hence it is optically inactive.]

28) Assign the primary valence and secondary valence of the central metal in $[Ni(CO)_4]$ (2)

Ans: Primary valence = 0

Secondary valence = 4

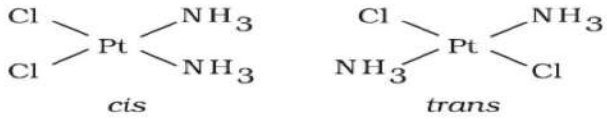
29) Cis isomer of $[Pt(NH_3)_2Cl_2]$ is used to inhibit the growth of tumors.

(a) Give the IUPAC name of $[pt\ (NH_3)_2Cl_2]$. (1)

(b) Give the structure of cis and trans isomers of $[Pt\ (NH_3)_2Cl_2]$. (2) *[March 2020]*

Ans: (a) Diamminedichloridoplatinum(II)

(b)



30) Write the IUPAC name of the following Co-ordination compounds :

(i) $[Co(NH_3)_6]Cl_3$ (ii) $K_3[Fe(C_2O_4)_3]$ (2)

Ans: (i) Hexaamminecobalt(III)chloride

(ii) Potassiumtrioxalatoferrate (III)

31) The octahedral complex $[Co(NH_3)_6]^{3+}$ is diamagnetic while $[CoF_6]^{3-}$ is paramagnetic. Explain using V.B. Theory. (3) *[SAY 2020]*

Ans: NH_3 is a strong field ligand and hence electron pairing occurs in $[Co(NH_3)_6]^{3+}$. So there is no unpaired electron and hence it is diamagnetic. While in $[CoF_6]^{3-}$, F^- is a weak field ligand and hence electron pairing does not occur. So there is unpaired electrons and hence it is paramagnetic.

32) (i) Write the IUPAC name of $K_2[Zn(OH)_4]$ (1)

(ii) Metal present in chlorophyll is ..... (1)

Ans: (i) Potassiumtetrahydroxidozincate(II)

(ii) Magnesium (Mg)

33) (i) Account for the following:

A. Zr and Hf have identical radii. (1)

B. Transition metals are very good catalysts. (1)

(ii) Calculate the spin only magnetic moment of $M^{2+}_{(aq)}$ ion (Z = 27). (1)

Ans: (i) A) Due to lanthanoid contraction/lanthanide contraction.

B) This is due to their large surface area and the ability to show variable oxidation state.

(ii) The electronic configuration of M^{2+} (Z = 27) is [Ar]$3d^7$. So the no. of unpaired electrons = 3.

The spin only magnetic moment, $\mu s = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

34) (i) List the various structural isomerism possible for co-ordination compounds. (2)

(ii) $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain. (2)

[March 2021]

Ans: (i) The different types of structural isomerism shown by co-ordination compounds are: 1. Ionisation isomerism 2. Linkage isomerism 3. Solvate or hydrate isomerism 4. Co-ordination isomerism.

(ii) H_2O is a weak field ligand and hence electron pairing does not occur while CN^- is a strong field ligand and hence electron pairing occurs. So the number of unpaired electrons in $[Fe(H_2O)_6]^{3+}$ greater than that in $[Fe(CN)_6]^{3-}$. Hence $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic. [Also refer the Ans. of the Question no. 15 (c)].

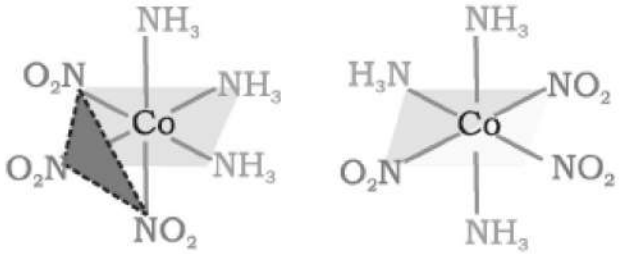
35) (i) Which among the following shows optical isomerism?

(A) $[Ni(CO)_4]$ (B) $[CoF_6]^{3-}$ (C) cis – $[Co(NH_3)_4Cl_2]^+$ (D) trans – $[Co(NH_3)_4Cl_2]^+$ (1)

(ii) Identify the geometrical isomers of $[Co(NH_3)_3Cl_3]$ and give their structures. (2)

Ans: (i) None [Octahedral complexes with unidentate ligands have plane of symmetry. So they do not show optical isomerism. Also tetrahedral complexes are symmetric. So $[Ni(CO)_4]$ is optically inactive].

(ii) $[Co(NH_3)_3Cl_3]$ shows facial – meridional (fac-mer) isomerism.



36) (i) Write the IUPAC name of $[Cr(H_2O)_6]Cl_3$. (1)

(ii) Explain linkage isomerism with a suitable example. (2) *[SAY 2021]*

Ans: (i) Hexaaquachromium(III)chloride

(ii) Linkage isomerism: It arises in a co-ordination compound containing ambidentate ligand, which can bind to the central atom through more than one donor atoms.

E.g. is $[Co(NH_3)_5(ONO)]Cl_2$ and $[Co(NH_3)_5(NO_2)]Cl_2$

37) (i) Describe the four types of structural isomerism exhibited by co-ordination compounds. (4)

(ii) Draw the geometrical isomers of $[Co(NH_3)_4Cl_2]^+$ (2) *[March 2022]*

Ans: (i) Co-ordination compounds show 4 types of structural isomerism:

*1) **Ionisation Isomerism**: It arises due to the inter change of ions between the inside and outside of co-ordination sphere. They give different types of ions in aqueous solution.*

An example is $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

*2) **Linkage isomerism:** It arises in a co-ordination compound containing ambidentate ligand, which can bind to the central atom through more than one donor atoms.*

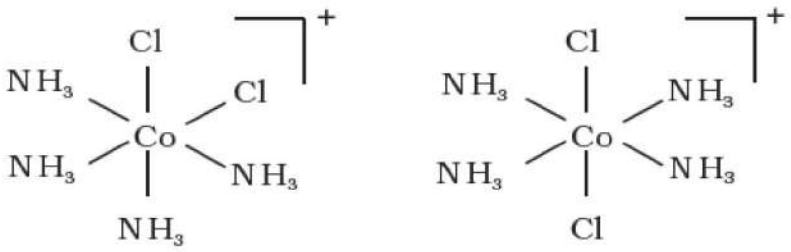
E.g. is $[Co(NH_3)_5(ONO)]Cl_2$ and $[Co(NH_3)_5(NO_2)]Cl_2$

*3) **Co-ordination Isomerism**: If both anionic and cationic parts are complexes, the isomerism arises due to the interchange of ligands between cationic and anionic entities. This type of isomerism is called co-ordination isomerism. An example is $[Co(NH_3)_6][Cr(CN)_6]$, and $[Cr(NH_3)_6][Co(CN)_6]$*

*4) **Solvate isomerism**: Solvate isomers differ in the no. of solvent molecule which are directly bonded to the metal ion as ligand.*

An example is $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

(ii)



cis *trans*

38) (i) What are the four different types of structural isomerism exist in co-ordination complexes? Explain with suitable examples. (4)

(ii) Give the IUPAC names of the following complexes: (a) $[Pt(NH_3)_2Cl_2]$ (b) $[Ni(CO)_4]$ (2) *[SAY 2022]*

Ans: (i) Refer the answer of the question no. 37 (a)

(ii) (a) Diamminedichloridoplatinum (II)

(b) Tetracarbonylnickel(0)

39) Give an example for a didentate ligand. (1)

Ans: Ethane-1,2-diamine OR, Ethylene diamine (H_2N-CH_2-CH_2-NH_2 (en) OR, Oxalate ion ($C_2O_4^{2-}$)

40) Write the IUPAC names of the following compounds : (a) $[Co(NH_3)_4(H_2O)Br]Br_2$ (b) $K_3[Al(C_2O_4)_3]$ (2)

Ans: (a) Tetraammineaquabromidocobalt (III) bromide

(b) Potassium trioxalatoaluminate (III)

41) (i) What is spectrochemical series ? (1)

(ii) Draw figure to show the splitting of d orbitals in octahedral crystal field and label the diagram. (2)

Ans: (i) It is a series in which the ligands are arranged in the increasing order of their field strength.

The series is: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$.

(ii) Refer the answer of Question no. 22

42) (i) Draw the structure of the geometrical isomers of the co-ordination compound $[Co(NH_3)_4Cl_2]^+$. (2)

(ii) On the basis of Valence Bond Theory, explain the structure and magnetic property of $[Ni(CN)_4]^{2-}$ (2)

[March 2023]

Ans: (i) Refer the answer of Question no. 37 (ii)

*(ii) In $[Ni(CN)_4]^{2-}$, the central atom Ni is in **dsp^2 hybridisation**. So it has a **square planar** geometry. Due to the absence of unpaired electrons, the complex is **diamagnetic.***

43) Name an ambidendate Ligand. (1)

Ans: Nitrito (N) $[NO_2^-]$ OR, cyanato $[CNO^-]$ OR, thiocyanato $[SCN^-]$

44) Write two Postulates of Werner's Coordination theory. (2)

Ans: Refer the answer of Question no. 14 (b)

45) (i) Define spectrochemical series. (1)

(ii) Diagrammatically represent the crystal field splitting of d-orbitals in a tetrahedral field. (2)

Ans: (i) Refer the answer of Question no. 41 (i)

(ii) Refer the answer of Question no. 12 (d)

46) (i) Which are the four types of structural isomerism exhibited by co-ordination compounds? (2)

(ii) Give one example for each type of Isomerism. (2)

[SAY 2023]

Ans: (i) Ionisation isomerism, Hydrate isomerism, Linkage isomerism and Co-ordination isomerism.

(ii) Refer the answer of Question no. 37 (i)

Haloalkanes and Haloarenes

1. a) You want to prepare $CH_3 - CH_2 - CH_2 - Br$ from $CH_3 - CH = CH_2$. What are the reagents you require? (1)

   b) $C_6H_5-CH_2-Cl$ can be converted to $C_6H_5-CH_2-OH$ by boiling with aqueous alkali. However C_6H_5-Cl cannot be converted to C_6H_5-OH by this method. Explain. (3) *[March 2008]*

   Ans: a) HBr and an organic peroxide like acetyl peroxide or benzoyl peroxide.

   b) C_6H_5-Cl is an aryl halide. Aryl halides do not readily undergo nucleophilic substitution reactions due to the following reasons:

   1. Resonance effect: Due to this effect, the C – X bond gets a partial double bond character.

   2. sp^2 hybridisation of the carbon to which halogen atom is bonded.

   3. Due to instability of phenyl cation, S_N2 reaction does not occur.

   4. due to repulsion between nucleophile and electron rich nucleophile.

2. a) $CH_3-CH_2-Br \xrightarrow{?} CH_3-CH_2-I$ (1)

   b) $CH_3-CH_2-CH_2-Br \xrightarrow{\text{Alc. KOH}} ?$ (1)

   c) Freons are known with respect to ozone layer depletion.

   i) What are freons? (1)

   ii) How can you prepare a Freon from CCl_4? (1) *[March 2009]*

   Ans: a) NaI

   b) $CH_3 - CH = CH_2$ [Propene]

   c) i) Chlorofluorocarbon compounds of methane and ethane are collectively known as freons.

   ii) Freon 12 (CCl_2F_2) is manufactured from CCl_4 by Swarts reaction. i.e. $CCl_4 + 2\ AgF \longrightarrow CCl_2F_2 + 2\ AgCl$

3. a) Most of the organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon – metal bonds.

   i) Give one example for such compound. (1)

   ii) How will you prepare the above compound? (1)

   b) How many chiral carbon and optical isomers are there for lactic acid? (1) *[March 2010]*

   Ans: a) i) A Grignard reagent CH_3MgBr (Methyl magnesium bromide)

   ii) *Methyl bromide reacts with magnesium metal in dry ether to form methyl magnesium bromide.*

   $CH_3-Br + Mg \xrightarrow{dry\ ether} CH_3MgBr$

   b) In lactic acid, there is only one chiral carbon. It has 2 optical isomers – dextro and laevo lactic acids.

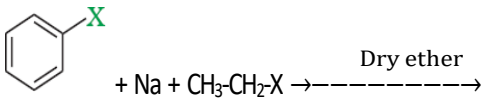
4. Haloalkanes and haloarenes react with metals to give hydrocarbons or products from which hydrocarbons are obtained easily.

   a) Identify the product and the name of the reaction:

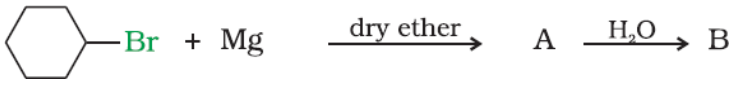
   (1)

   b) Identify the product and the name of the reaction:



(1)

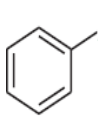
c) Identify A & B.



(2) *[March 2011]*

Ans: a) Diphenyl or biphenyl. The reaction is known as Fittig reaction.

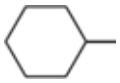
b)



[Ethyl benzene]. The reaction is known as Wurtz-Fittig reaction.

c) A is cyclohexylmagnesium bromide and B is cyclohexane

i.e.

A is  *MgBr* *B is* 

5. Alkyl halides are the starting materials for the synthesis of a number of organic compounds. How are the following compounds obtained from alkyl halide CH_3-CH_2-Br?

a) Ethane (1)

b) Ethanol (1)

c) Butane (1)

d) Ethoxyethane (1) *[SAY 2011]*

Ans: a) CH_3-CH_2-Br $\xrightarrow[Alc.\ KOH]{LiAlH_4}$ $CH_3 - CH_3$ *[Reduction with LIAlH$_4$]*

b) CH_3-CH_2-Br $\longrightarrow$ $CH_3 - CH_2 - OH$ *[Treating with aqueous KOH]*

c) $2\ CH_3$-CH_2-Br + 2 Na $\xrightarrow{Dry\ ether}$ $CH_3 - CH_2 - CH_2 - CH_3$ *[Treating with metallic sodium in dry ether]*

d) CH_3-CH_2-Br + $CH_3 - CH_2 - ONa$ $\longrightarrow$ CH_3-CH_2-O-CH_2-CH_3 *[Treating with sodium ethoxide]*

6. Nucleophilic substitution reactions are of two types – S_N1 reactions and S_N2 reactions.

i) Write any 2 differences between S_N1 and S_N2 reactions. (2)

ii) Write any 2 reasons for the less reactivity of aryl halides towards nucleophilic substitution reactions (2) *[March 2012]*

Ans: i)

S_N1 Reaction	***S_N2 Reaction***
Proceeds in 2 steps	*Proceeds in a single step*
An intermediate (carbocation) is formed	*No intermediate is formed*
Order of the reaction is 1	*Order is 2*
For optically active compounds, the reaction proceeds through racemisation.	*For optically active compounds, the reaction proceeds through inversion of configuration.*
The order of reactivity of alkyl halide is $3^0 > 2^0 > 1^0$	*The order of reactivity of alkyl halide is $1^0 > 2^0 > 3^0$*

[Any 2 Differences required]

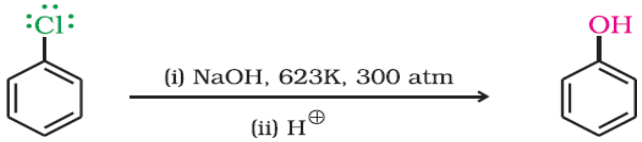
ii) Refer the Answer of Question no. 1 (b)

7. Haloarenes undergo nucleophilic and electrophilic substitution reactions.
   a) Write two examples for ambident nucleophiles. (1)
   b) Write one example for nucleophilic substitution reaction of chlorobenzene. (1)
   c) Write any 2 examples of electrophilic substitution reaction of chlorobenzene. (2) *[SAY 2012, 2013 & March 2010]*

Ans: a) CN^- and NO_2^-

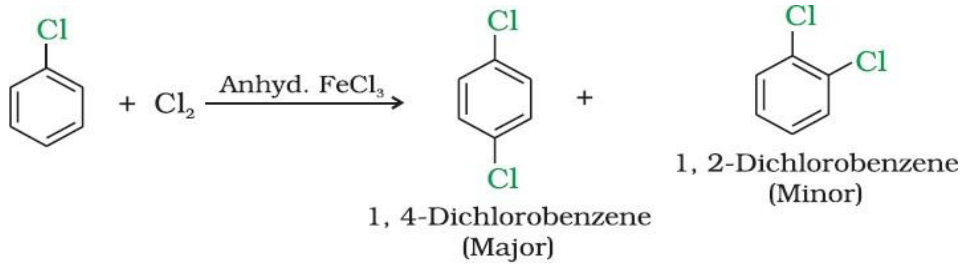
b) Chlorobenzene when heated with aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres followed by acidification, we get phenol.

Or, the equation:



c) Electrophilic substitution reactions of chlorobenzene are:

i) Halogenation:



ii) Nitration:

8. a) For the preparation of alkyl chlorides from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason. (1)
   b) Halo alkanes undergo β-elimination reaction in presence of alcoholic potassium hydroxide.
      i) Which is the major product obtained by the β-elimination of 2-bromo pentane. (½)
      ii) Name the rule, which leads to the product in the above elimination reaction. (1)
   c) Write the chemical equation for the preparation of toluene by Wurtz-Fittig reaction. (1½)

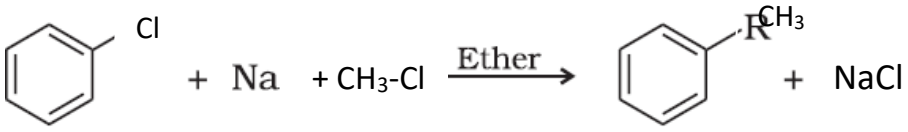
[March 2013]

Ans: a) When thionyl chloride is used, we get pure alkyl chlorides, since the bi-products are gases.

b) (i) Pent-2-ene ($CH_3 – CH_2- CH = CH- CH_3$)

(ii) Saytzeff's rule or Zaitsev's rule.

c)



Chlorobenzene *Toluene*

9. a) i) Write 'Saytzeff rule' (1)

ii) The products A and B of the following reaction are two isomeric alkenes. Identify A & B.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH(Br)\text{-}CH_3 \xrightarrow{\text{Alc. KOH}} A + B$

b) Identify the main products of the following reactions? Suggest whether the reaction is S_N1 or S_N2?

i) $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}} - CH_3 \xrightarrow{\text{aq. NaOH}}$

ii) $C_6H_5 - CH_2 - Br \xrightarrow{\text{aq. NaOH}}$ (2) *[SAY 2013]*

Ans: a) i) The rule states that in dehydrohalogenation reactions, the major product is that alkene which contains greater number of alkyl groups attached to the doubly bonded carbon atoms.

ii) A is pent-2-ene and B is pent-1-ene.

b) i) tert-butyl alcohol [$(CH_3)_3C\text{-}OH$]. The reaction is S_N1

ii) $C_6H_5 - CH_2 - OH$. The reaction is S_N1.

10. a) Most important chemical reactions of halo alkanes are their substitution reactions.

i) What is S_N1 reaction? (1)

ii) Arrange the four isomeric bromobutanes in the increasing order of reactivity towards S_N1 reaction. (2)

b) How will you prepare chlorobenzene from benzene diazonium chloride? (1) *[March 2014]*

Ans: a) i) It is unimolecular nucleophilic substitution reaction.

ii) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br < (CH_3)_2CH - CH_2\text{-} Br < CH_3 - CH(Br) - CH_2\text{-} CH_3 < (CH_3)_3C - Br$

(n-butyl bromide) (isobutyl bromide) (sec- butyl bromide) (tert- butyl bromide)

b) When benzene diazonium chloride is treated with HCl in presence of cuprous chloride (Cu_2Cl_2), we get a chlorobenzene. This reaction is called Sandmeyer's reaction.

$C_6H_5N_2^+Cl^- + HCl \xrightarrow{Cu_2Cl_2} C_6H_5\text{-}Cl + N_2 + HCl$

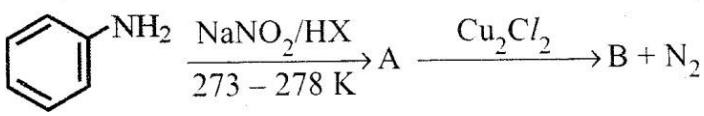
11. a) Among the following which one is chlorine containing insecticide?

i) DDT ii) Freon iii) Phosgene iv) Iodoform (1)

b) Haloarenes undergo Wurtz-Fittig reaction.

i) What is Wurtz-Fittig reaction? (1)

ii)



Write the formulae of A and B in the above reaction. (2) *[March 2015]*

Ans: a) DDT

b) (i) When a mixture of alkyl halide and aryl halide is treated with sodium in dry ether, an alkyl arene is formed and this reaction is called Wurtz-Fittig reaction.

(ii) A is benzene diazonium chloride ($C_6H_5N_2^+Cl^-$) and B is chlorobenzene ($C_6H_5 - Cl$).

12. i) State Saytzeff rule. (1)

ii) Identify the major and minor products obtained by the reaction between 2-bromobutane and alcoholic KOH. (1)

iii) Write the product obtained by the reaction between 2-bromobutane and aqueous KOH. (1)

iv) 2-Bromobutane exhibit optical isomerism. What is optical isomerism? (1) *[SAY 2015]*

Ans: i) Refer the Answer of Question no. 9 a) (i)

ii) Major product is but-2-ene and the minor product is but-1-ene.

iii) Butan-2-ol

iv) The phenomenon of rotation of the plane of polarised light by certain molecules is termed as optical isomerism.

13. Aryl halides are less reactive in nucleophilic substitution reactions.

a) i) Write any two reasons for less reactivity. (1)

ii) Give one example for nucleophilic substitution reactions of aryl halides. (1)

b) Write a method for the preparation of alkyl halides.

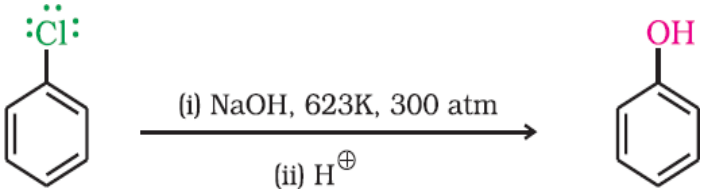
c) Which of the following is not a polyhalogen compound?

(a) Chloroform (b) Freon (c) Carbon tetrachloride (d) Chloro benzene (1) *[March 2016]*

Ans: a) (i) Resonance effect and instability of phenyl cation.

(ii) Chlorobenzene when heated with aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres followed by acidification, we get phenol.

Or, the equation:



b) Addition of hydrogen halide to alkene.

c) Chlorobenzene

14. Haloalkanes and haloarenes are compounds containing halogen atom. They undergo many types of reactions.

a) Identify the product formed in the following reaction:

$$CH_3\text{-}CH_2\text{-}CH_2Cl \xrightarrow{\text{Alc. KOH}}$$

i) $CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$ ii) $CH_3\text{-}CH(OH)\text{-}CH_3$ iii) $CH_3\text{-}CH{=}CH_2$ iv) $CH_3\text{-}C{\equiv}CH$ (1)

b) i) Chloroform is stored in closed, dark coloured bottles completely filled up to the neck. Give reason. (1)

Ans: a) CH_3-CH=CH_2

b) To avoid the oxidation of chloroform to the poisonous compound phosgene.

15. Write any two differences between S_N1 and S_N2 reactions. (2) *[SAY 2016]*

Ans: Refer the Answer of Question no. 6 (i)

16. a) An ambident nucleophile is:

i) Ammonia ii) Ammonium ion iii) Chloride ion iv) Nitrite ion (1)

b) Haloalkanes and haloarenes are organohalogen compounds.

i) Suggest a method for the preparation of alkyl chloride. (1)

ii) Aryl halides are less reactive towards Nucleophilic substitution reactions. Give reason. (2)

[March 2017]

Ans: a) Nitrite ion

(b) (i) Alkyl chlorides can be prepared by the reaction between alcohols with hydrogen chloride in presence of anhydrous $ZnCl_2$ or by the reaction between alcohol and PCl_3 or PCl_5 or $SOCl_2$.

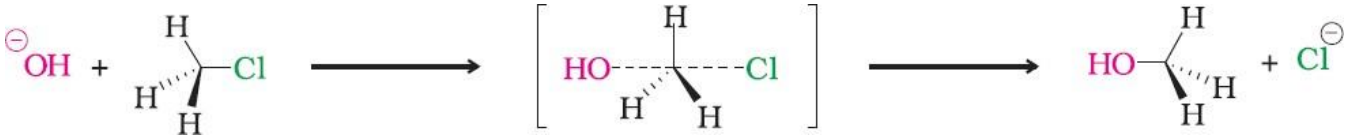
(ii) Refer the Answer of Question no. 1(b)

17. On kinetic consideration nucleophilic substitution in aryl/alkyl halides may be S_N1 or S_N2 mechanisms.

a) Briefly explain S_N2 mechanism with an example. (2)

b) In dehydrohalogenation of 2-Bromopentane why Pent-2-ene is major product and Pent-1-ene is minor product. (2) *[SAY 2017]*

Ans: a) Here the incoming nucleophile interacts with alkyl halide causing the carbon-halogen bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed.



b) According to zaitsev's rule, the major product is that alkene which contains greater number of alkyl groups around C = C bond. Here pent-2-ene contains greater no. of alkyl groups around C = C bond and so it is the major product.

18. During the B-elimination reaction of 2-bromopentane in an alcoholic solution of KOH results Pent-2-ene as the major product and pent-1-ene as the minor product. State the rule to explain the reaction. (2)

Ans: Refer the Answer of Question no. 9 a) (i)

19. Complete the reactions:

(a) $CH_3CH_2Br \xrightarrow{AgCN} \ldots\ldots\ldots\ldots$

(b) $CH_3CH_2Br \xrightarrow{Na\ /\ Dry\ ether} \ldots\ldots\ldots\ldots$ (2) *[March 2018]*

Ans: (a) $CH_3 - CH_2 - NC$

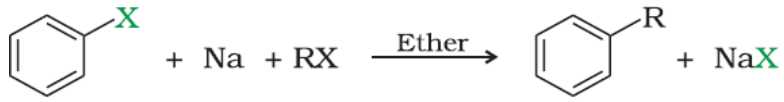
(b) CH_3- CH_2- CH_2- CH_3

20. Give one use each of Freon 12, DDT, CCl_4 and CHI_3. (2)

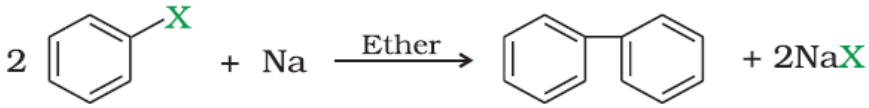
Ans: Freon 12 – as a refrigerant, DDT – as an insecticide, CCl_4 – as a solvent, CHI_3 – as an antiseptic.

21. Write equations showing Wurtz-Fittig reaction and Fittig reaction. (2) *[SAY 2018]*

Ans: Wurtz-Fittig reaction:



Fittig reaction:



22. 2-Bromobutane is optically active. Explain the stereo-chemical aspect of S_N^1 reaction of 2-Bromobutane with OH^- ions. (2)

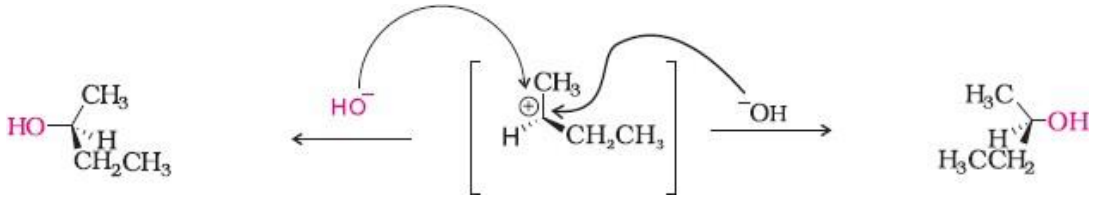
Ans: a) S_N1 reaction of optically active 2-bromobutane with OH^- results in the formation of a racemic mixture of (±) 2-butanol.

$$CH_3 - CHBr - CH_2 - CH_3 \xrightarrow{OH^-} CH_3 - CHOH - CH_2 - CH_3 + Br^-$$

Mechanism:

Step – I

Step – II



(-) 2-butanol *Planar carbocation* *(+) 2-butanol*

23. How can the following conversions be effected?

(i) Ethanol to Fluoroethane (2)

(ii) But-1-ene to But-2-ene (2) *[March 2019]*

Ans: i) $CH_3\text{-}CH_2\text{-}OH + PCl_3\ (PCl_5 \text{ or } SOCl_2) \longrightarrow CH_3\text{-}CH_2\text{-}Cl \xrightarrow{AgF/SbF_3/CoF_2/Hg_2F_2} CH_3\text{-}CH_2\text{-}F$

ii) $CH_3\text{-}CH_2\text{-}CH = CH_2 \xrightarrow{HBr} CH_3\text{-}CH_2\text{-}CHBr\text{-}CH_3 \xrightarrow{Alc.\ KOH} CH_3\text{-}CH{=}CH\text{-}CH_3$

(In the first step HCl or HI can also be used).

24. Explain S_N^1 mechanism with suitable examples. (3)

Ans: Refer the Answer of Question no. 22

25. Write the reaction of ethyl bromide with the following reagents :

(a) aq. KOH (b) KCN (c) AgCN (3) *[SAY 2019]*

Ans: (a) CH_3-CH_2-Br + aq. KOH →−−−−→ CH_3-CH_2-OH

(b) CH_3-CH_2-Br + KCN →−−−−→ CH_3-CH_2-CN

(c) CH_3-CH_2-Br + AgCN →−−−−→ CH_3-CH_2-NC

26. In the presence of light, chloroform is slowly oxidised by air to an extremely poisonous gas called ……. (1)

Ans: Phosgene or Carbonyl chloride ($COCl_2$)

27. Aryl halides are less reactive towards nucleophilic substitution reactions. Write any two reasons for the less reactivity of aryl halides. (2)

Ans: Refer the Answer of Question no. 1 (b)

28. (a) Which is the major product obtained when 2-bromopentane is heated with alcoholic solution of potassium hydroxide? (1)

(b) Name and state the rule that governs the formation of major product. (2) *[March 2020]*

Ans: Refer the Answer of Question no. 8 (b) and 9 (a)

29. Among the halogen derivatives of ethane, the one which has the highest boiling point:

(a) C_2H_5F (b) C_2H_5Cl (c) C_2H_5I (d) C_2H_5Br (1)

Ans: C_2H_5I

30. (a) Name a polyhalogen compound used as an insecticide. (1)

(b) Why chloroform is kept in dark coloured bottles? (1)

Ans: a) DDT

b) To avoid the oxidation of chloroform to the poisonous compound phosgene.

31. (a) Write difference between S_N1 and S_N2 reactions. (2)

(b) How will you convert ethyl chloride to ethyl cyanide? (1) *[SAY 2020]*

Ans: a) Refer the Answer of Question no. 6 (i)

b) By treating with KCN. CH_3-CH_2-Br + KCN →−−−−→ CH_3-CH_2-CN

32. Identify the main product in the following reactions:

(i) CH_3-CH_2-OH $\xrightarrow{PCl_3}$ (1)

(ii) CH_3 - CH = CH_2 $\xrightarrow{HI}$ (1)

Ans: i)CH_3-CH_2-Cl (Ethyl chloride)

ii) CH_3 – CHI - CH_3 (2-Iodopropane)

33. (i) Give two differences between S_N1 and S_N2 reactions. (2)

(ii) Arrange 1-chloropropane, 2-chloropropane and 1-chlorobutane in the increasing order of their boiling points. (1)

(iii) Give one use of chloroform. (1) *[March 2021]*

Ans: (i) Refer the Answer of Question no. 6 (i)

(ii) 2-chloropropane < 1-chloropropane < 1-chlorobutane

(iii) Chloroform is used as a solvent, for the production of freon refrigerant, as an anaesthetic etc.

[Any 1 use is required]

34. How can 'propene' be converted into '2-Bromopropane'? (2)

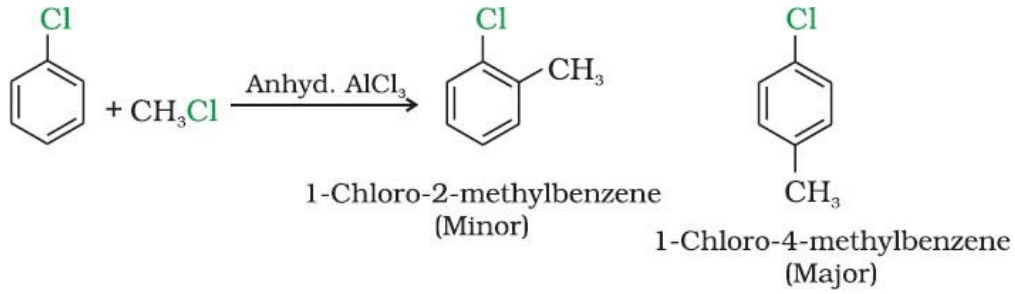
Ans: By treating with HBr

CH_3-CH = CH_2 + HBr →−−−−→ CH_3-CHBr-CH_3 (Major product)

35. (i) How is chlorobenzene converted into 1-chloro-4-methyl benzene? (2)

(ii) Haloarenes are less reactive towards nucleophilic substitution. Why? (2) *[SAY 2021]*

Ans: (i) By Friedel – Craft's alkylation reaction. i.e. Chlorobenzene is treated with CH_3-Cl in presence of anhydrous $AlCl_3$, we get 1-chloro-4-methyl benzene as the major product.



36. The reaction which converts benzene diazonium chloride to chlorobenzene using CuCl in HCl is known as -…….

(a) Swarts reaction (b) Sandmeyer's reaction (c) Finkelstein reaction (d) Kolbe's reaction (1)

Ans: Sandmeyer's reaction

37. (i) Write a suitable method to convert $CH_3–CH_2–Br$ to $CH_3–CH_2–I$ (1)

(ii) Suggest and explain a suitable mechanism for the nucleophilic substitution of tert-butyl bromide with NaOH. (2)

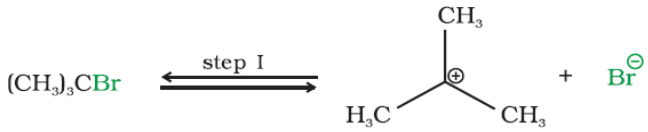
Ans: (i) By treating with sodium iodide (NaI) in dry acetone. [Finkelstein reaction]

OR, CH_3-CH_2-Br + NaI →−−−−→ CH_3-CH_2-I + NaBr

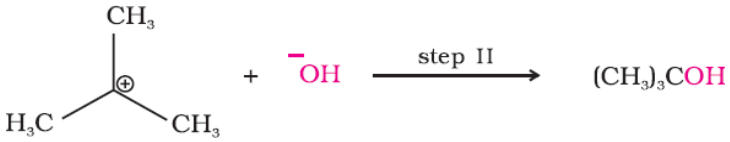
(ii) S_N1 mechanism (Substitution nucleophilic unimolecular mechanism)

The reaction occurs through 2 steps:

Step 1: Formation of carbocation:



Step 2: The carbocation is attacked by the nucleophile (OH-) to form the product.



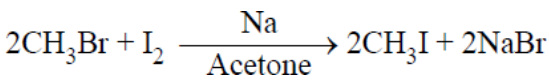
38. (i) What are Grignard reagents? (1)

(ii) State Saytzeff rule and illustrate it with an example. (2) *[March 2022]*

Ans: (i) Alkyl magnesium halide [R-MgX]

(ii) Refer the Answer of the Question number 9 (a).

39.

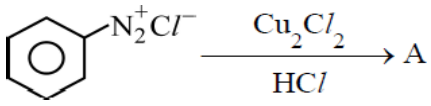


Name of this reaction is:

(i) Grignard reaction (ii) Swarts reaction (iii) Finkelstein Reaction (iv) Gattermann reaction (1)

Ans: Finkelstein reaction

40. (i) Complete the following reaction :



(1)

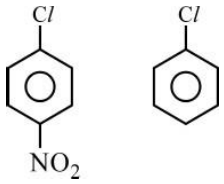
(ii) Explain Wurtz Fittig reaction with an example. (2)

Ans: (i) Chlorobenzene

(ii) Refer the Answer of the Question number 11 (b).

41. (i) How will you convert chlorobenzene to phenol? (1)

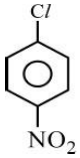
(ii) Which of the following is more reactive?



Justify your answer. (2) *[SAY 2022]*

Ans: (i) Refer the Answer of the Question number 7 (b)

(ii)



is more reactive

This is because the presence of nitro group at para-position withdraws the electron density from the benzene ring and thus the attack of the nucleophile becomes easier.

42. $CH_3\text{-}CH_2\text{-}Br + NaI \xrightarrow[\text{Dry acetone}]{} CH_3 - CH_2 - I + NaBr$. The name of this reaction is ..... (1)

Ans: Finkelstein reaction

43. Differentiate between S_N1 and S_N2 reactions. (2)

Ans: Refer the Answer of Question no. 6 (i)

44. (i) Identify the major and minor product obtained by the reaction between 2-bromobutane and alcoholic KOH. (2)

(ii) Name and state the rule behind the formation of these products. (2) *[March 2023]*

Ans: (i) But-2-ene [$CH_3\text{-}CH=CH\text{-}CH_3$]

(ii) Zaitsev's rule. The rule states that in dehydrohalogenation reaction, the major product is that alkene which contains greater number of alkyl groups around C = C bond.

45. Which among the following will undergo S_N2 reaction faster ?

(a) $CH_3–CH_2–CH_2Cl$ (b) $CH_3–CHCl–CH_3$ (c) $(CH_3)_3CCl$ (d) $CH_3–CHCl–CH_2–CH_3$ (1)

Ans: (a) $CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$

46. State Zaitsev Rule. (2)

Ans: Refer the Answer of the Question number 44 (ii)

47. Describe the following :

(i) Sandmeyers Reaction (2)

(ii) Fittig Reaction (1)

(iii) Wurtz-Fittig Reaction (1) *[SAY 2023]*

Ans: (i) Refer the Answer of the Question number 10 (b)

(ii) & (iii) Refer the Answer of Question no. 21.

Alcohols, Phenols and Ethers

1. The bond angle in C-O-H in alcohols is slightly less than tetrahedral angle.
   a) Give the reason for the difference in the bond angle observed in alcohol. (1)
   b) What is the bond angle in C-O-H in phenol? Give the reason for the variation. (2)
   c) Alcohols undergo dehydration. How is ethanol converted to ethene? (1) *[March 2008]*

   Ans: a) It is due to the repulsion between the 2 unshared electron pairs of oxygen.

   b) The C-O-H bond angle in phenol is 109^0. It is due to the repulsion between unshared electron pair on oxygen atom and due to the presence of bulky phenyl group.

   c) Ethanol on heating with concentrated H_2SO_4 at 443 K, undergoes dehydration to form ethene.

   $$CH_3\text{-}CH_2\text{-}OH \xrightarrow{H_2SO_4/443\ k} CH_2{=}CH_2 + H_2O$$

2. Williamson's synthesis is an important method of ether synthesis.
   a) To synthesis tertiary butyl ether, which of the following reagent sets are better? Justify.
      i) $(CH_3)_3C\text{-}Br + CH_3ONa$
      ii) $(CH_3)_3C\text{-}ONa + CH_3\text{-}Br$. (2)
   b) Explain the cleavage of C-O in $CH_3\text{-}CH_2\text{-}O\text{-}CH_3$ when treated with HI. (1) *[March 2009]*

   Ans: a) The set of reagents $(CH_3)_3C\text{-}ONa$ & $CH_3\text{-}Br$ are suitable for the preparation of tert-butyl ether. If the alkoxide used is primary, dehydrohalogenation occurs and the product formed is an alkene. This is because of the strong basic character of 1^0 alkoxide.

   b) In the case of ethers containing two different alkyl groups, the lower alkyl group forms the alkyl halide.

   $$CH_3\text{-}O\text{-}CH_2\text{-}CH_3 + HI \longrightarrow CH_3\text{-}I + CH_3\text{-}CH_2\text{-}OH$$

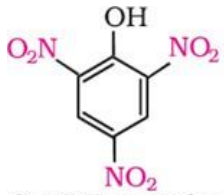
3. Phenols are more acidic than alcohols.
   a) Name the product obtained when phenol is treated with chloroform in the presence of NaOH. (½)
   b) Name the above reaction. (½)
   c) What is the product obtained when phenol is treated with Conc. HNO_3? (½)
   d) Write the structure and IUPAC name of the above product. (1)
   e) Ethanol and propane have comparable molecular masses, but their boiling points differ widely. Which of them have higher boiling points? Substantiate your answer. (1½) *[March 2010]*

   Ans: a) Salycylaldehyde (o-hydroxybenzaldehyde)

   b) Reimer-Tiemann reaction

   c) Picric acid

   d) 2,4,6-trinitrophenol



2,4,6-Trinitrophenol

   e) Ethanol has higher boiling point than propane. This is due to inter molecular hydrogen bonding in ethanol.

4. Ethanol can be prepared by treating HCHO and CH_3CH_2MgBr.
   a) Is the above statement true? (1)
   b) Justify your answer. (2) *[March 2010]*

   Ans: a) This is not true.

   b) For the preparation of ethanol, treat formaldehyde (HCHO) with methyl magnesium bromide (CH_3MgBr).

   $$H\text{-}CHO + CH_3MgBr \longrightarrow CH_3\text{-}CH_2\text{-}OMgBr \xrightarrow{H_2O} CH_3\text{-}CH_2\text{-}OH + MgBr(OH)$$

5. Ethers are generally non-reactive compounds. One of the important reactions of ethers is the action of HI.

   $$C_6H_5\text{-}O\text{-}CH_3 \xrightarrow{HI} A + B$$

   Identify A and B. explain the reaction. (4) *[March 2011]*

   Ans: A is phenol (C_6H_5-OH) and B is iodomethane (CH_3-I)

   $$C_6H_5\text{-}O\text{-}CH_3 \xrightarrow{HI} C_6H_5\text{-}OH + CH_3\text{-}I$$

   Here the O-CH_3 bond is weaker than the O–C_6H_5 bond. This is because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character.

6. Mixture of Conc. HCl and anhydrous $ZnCl_2$ is an important reagent which helps to distinguish between 1^0, 2^0 and 3^0 alcohols.
   a) Give the name of the above reagent. (½)
   b) Give one example each for 1^0, 2^0 and 3^0 alcohols. (1½)
   c) Explain how the above reagent helps to distinguish above three types of alcohols. (2) *[SAY 2011]*

   Ans: a) Lucas Reagent

   b) 1^0 alcohol – methanol (CH_3-OH), 2^0 alcohol – isopropylalcohol [$(CH_3)_2CHOH$] and 3^0 alcohol – tert-butyl alcohol [$(CH_3)_3C$-OH]

   c) Lucas Test: Tertiary alcohols react with Lucas reagent and form immediate turbidity; secondary alcohols form a turbidity within 5 minutes while primary alcohols do not produce turbidity at room temperature. But they give turbidity on heating.

7. a) Write the name or structure of the compounds A and B in the following reactions:

   $$A \xleftarrow[H^+]{CHCl_3 + NaOH} C_6H_5OH \xrightarrow[H^+]{NaOH/CO_2} B$$

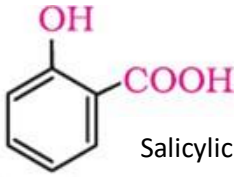
   (2)

   b) Vapours of an alcohol 'C' on passing over heated copper produce compound 'D'. 'D' on reaction with CH_3MgCl followed by hydrolysis produces 2-methylbutan-2-ol. Write the name or structure of compounds 'C' and 'D'. (2) *[March 2012]*

   Ans: a) A is salicylaldehyde and B is salicylic acid

   Salicylaldehyde

   Salicylic Acid

   b) C is butan-2-ol and D is butanone.

$$CH_3\text{-}CH_2\text{-}CHOH\text{-}CH_3 \xrightarrow{hot\ Cu} CH_3\text{-}CH_2\text{-}CO\text{-}CH_3 \xrightarrow{CH_3MgCl/H_2O} CH_3 - CH_2 - \underset{CH_3}{\overset{OH}{C}} - CH_3$$

Butan-2-ol Butanone

8. Methanol and ethanol are two commercially important alcohols.
   i) Write one method of preparation of methanol and ethanol. (2)
   ii) Name the products obtained when ethanol is treated with CrO_3 in anhydrous medium. (1)
   iii) The boiling point of ethanol is higher than that of methoxy methane. Give reason. (1) *[SAY 2012]*

Ans: i) Formaldehyde on reduction using $LiAlH_4$, gives methanol, while acetaldehyde gives ethanol.

$$R\text{-}CHO + [H] \xrightarrow{LiAlH_4} R\text{-}CH_2OH$$

$$R_2CO + [H] \xrightarrow{LiAlH_4} R_2CH\text{-}OH$$

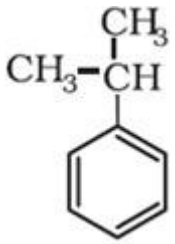
ii) Ethanal or acetaldehyde $[CH_3\text{-}CH_2\text{-}OH \xrightarrow{CrO_3} CH_3\text{-}CHO]$

iii) This is due to the presence of inter molecular hydrogen bonding in ethanol.

9. a) Write the IUPAC names of all the possible isomers with molecular formula C_3H_8O (1½)
   b) Phenol is usually manufactured from cumene. Write the structure of cumene. (½)
   c) Primary, secondary and tertiary alcohols can be distinguished by Lucas test.
   i) What is Lucas reagent? (½)
   ii) Write the observations, for primary, secondary and tertiary alcohols in Lucas test. (1½) *[March 2013]*

Ans: a) $CH_3\text{-}CH_2\text{-}CH_2OH$:– Propan-1-ol, $CH_3\text{-}CHOH\text{-}CH_3$:– Propan-2-ol and $CH_3\text{-}O\text{-}CH_2\text{-}CH_3$:– Methoxyethane

b) Cumene is isopropylbenzene (2-phenyl propane). Its structure is:



c) i) Lucas reagent is a mixture of Conc. HCl and anhydrous $ZnCl_2$

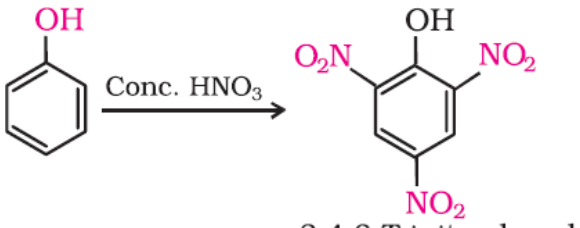
ii) Tertiary alcohols react with Lucas reagent and form immediate turbidity; secondary alcohols form turbidity within 5 minutes while primary alcohols do not produce turbidity at room temperature.

10. How are the following conversions carried out? Represent the chemical reactions.
    a) Ethanol to ethanal (1)
    b) Phenol to picric acid (1)
    c) Phenol to benzene (1)
    d) Phenol to tribromophenol (1) *[June 2013]*

Ans: a) By oxidation using CrO_3.

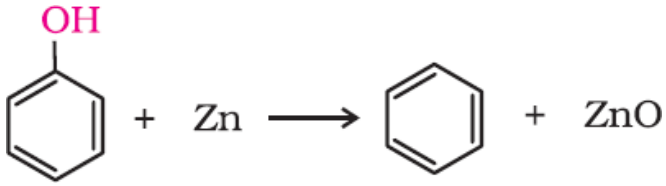
$$CH_3\text{-}CH_2\text{-}OH \xrightarrow{CrO_3} CH_3\text{-}CHO$$

b) By nitration using nitrating mixture.

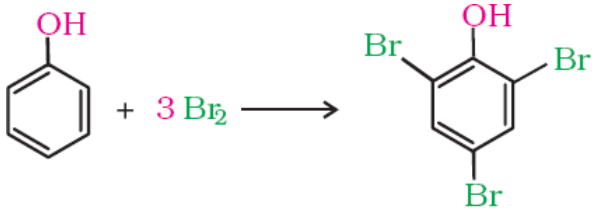


2,4,6-Trinitrophenol
(Picric acid)

c) By heating with zinc dust.



d) Bromination using bromine water.



2,4,6-Tribromophenol

11.a) How will you prepare the following compounds using a Grignard reagent?

i) Primary alcohol

ii) Secondary alcohol (2)

b) How will you distinguish primary and secondary alcohols using Luca's test? (1)

c) Write the correct pair of reactants for the preparation of t-butyl methyl ether by Williamson synthesis. (1) *[March 2014]*

Ans: a) Formaldehyde (methanal) reacts with Grignard reagent followed by hydrolysis gives primary alcohols.

$H\text{-}CHO + RMgX \longrightarrow R\text{-}CH_2\text{-}OMgX \xrightarrow{H_2O} R\text{-}CH_2\text{-}OH + MgX(OH)$

Formaldehyde — adduct — 1^0 alcohol

Aldehydes other than formaldehyde, react with Grignard reagent followed by hydrolysis gives secondary alcohols.

$R\text{-}CHO + RMgX \longrightarrow R_2CHOMgX \xrightarrow{H_2O} R_2CHOH + MgX(OH)$

Aldehyde — adduct — 2^0 alcohol

b) Refer the answer of question no. 6 (c).

c) Refer the answer of question no. 2 (a).

12. a) Write the name or formula of the following:

i) A simple ether

ii) A mixed ether

iii) A dihydric alcohol

iv) A trihydric alcohol (2)

b) Phenol on treatment with Br_2 in CS_2 at low temperature gives two isomeric monobromophenols 'X' and 'Y'. But phenol on treatment with bromine water gives a white precipitate 'Z'. Identify the products 'X', 'Y' and 'Z'. (2) *[SAY 2014]*

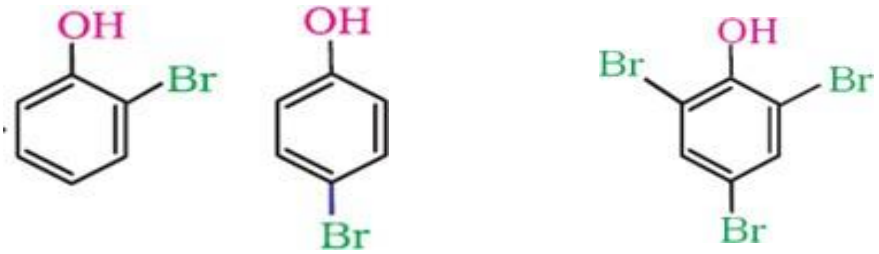
Ans: a) i) $CH_3 - O - CH_3$ (Methoxymethane)

ii) CH_3-CH_2-O-CH_3 (Methoxyethane)

iii) HO-CH_2-CH_2-OH (Ethane-1,2-dial)

iv) HO-CH_2-CHOH-CH_2OH (Propane-1,2,3-trial)

b) X is 2-Bromophenol, Y is 4-Bromophenol and Z is 2,4,6-tribromophenol.



X = o-bromophenol Y= p-bromophenol Z = 2,4,6-tribromophenol

13. Alcohols are compounds with general formula R-OH.

a) Alcohols are soluble in water. Give reason? (1)

b) i) Explain a method for the manufacture of ethanol. (2)

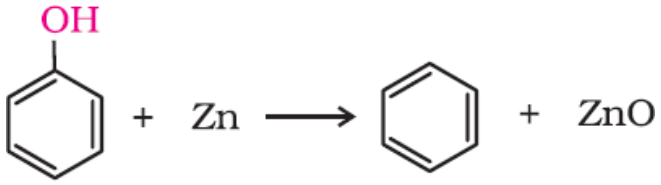
ii) How will you convert phenol to benzene? (1) *[March 2015]*

Ans: a)This is because alcohols can form inter molecular hydrogen bonding with water.

b) i) Ethanol can also be manufactured by hydration of ethene in acidic medium.

$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3\text{-}CH_2\text{-}OH$$

ii) By heating with zinc dust.



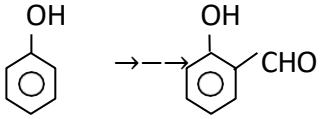
Phenol Benzene

14. a) Write a test to distinguish between phenol and alcohol. (1)

b) Write suitable reagent(s) used for the following conversions:

i) CH_3-CH_2-Cl →—→ CH_3-CH_2-OH

ii) CH_3-CH_2-OH →—→ CH_3-CH_2-O-CH_2-CH_3

iii) 

(3) *[SAY 2015]*

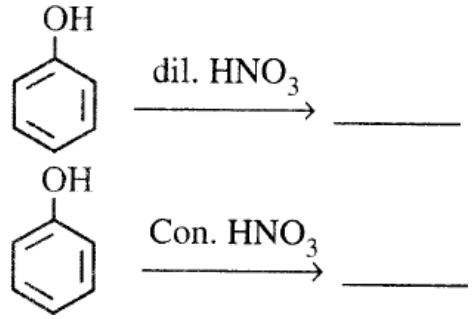
Ans: a) Phenol gives a white precipitate with bromine water, but alcohol does not. [Phenol gives a violet colouration with neutral ferric chloride, while alcohol does not].

i) Aq. KOH or NaOH

ii) Conc. H_2SO_4/413 K

iii) Chloroform ($CHCl_3$) + aq. NaOH followed by acidification

15.a) Complete the following:



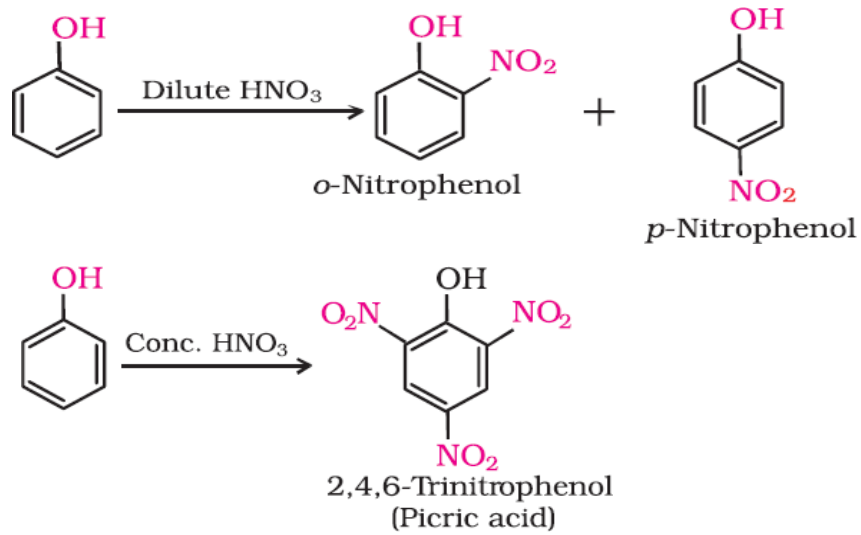
(2)

b) Explain the following:

i) Esterification

ii) Williamson Synthesis (2) *[March 2016]*

Ans: a)



b) i) Esterification: Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

ii) Williamson Synthesis: Alkyl halide reacts with sodium alkoxide to form ether. This reaction is called Williamson's ether synthesis.

R-X + R'-ONa → R-O-R' + NaX

16. a) Phenol when treated with Conc. HNO_3 gives,

(i) o-Nitrophenol (ii) p-Nitrophenol (iii) 2,4,6-Trinitrophenol (iv) a mixture of o-nitrophenol and p-nitrophenol (1)

b) Methanol and ethanol are two commercially important alcohols. Write one method each for the preaparation of methanol and ethanol. (3) *[SAY 2016]*

Ans: a) 2,4,6-Trinitrophenol

b) Refer the answer of question no. 8 (i)

17. a) Arrange the following compounds in the order of increasing boiling points:

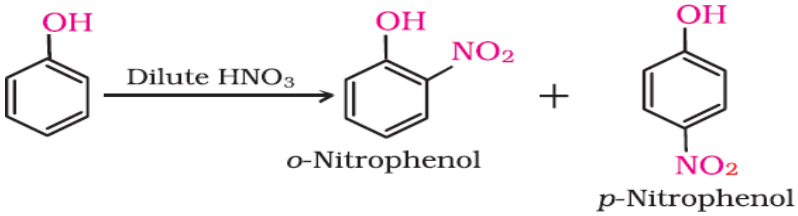
Ethanol, Propan-1-ol, Butan-1-ol, Butan-2-ol (1)

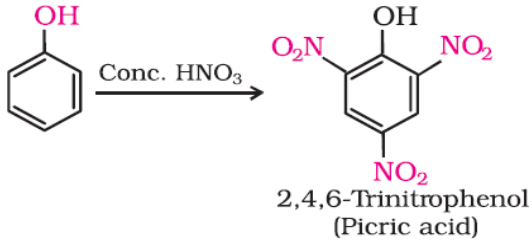
b) In the lab, students were asked to carry out the reaction between phenol and conc. HNO_3. But one student, 'A' carry out the reaction between phenol and dil. HNO_3. Do you think the student 'A' got the

same result as others. Substantiate with suitable explanations. [also write the chemical equations wherever necessary]. (3) *[March 2017]*

Ans: a) Ethanol < Propan-1-ol < Butan-2-ol < Butan-1-ol

b) With dil. HNO_3, phenol gives a mixture of ortho and para nitrophenols, but with conc. HNO_3, it gives 2,4,6 –trinitrophenol (Picric acid)



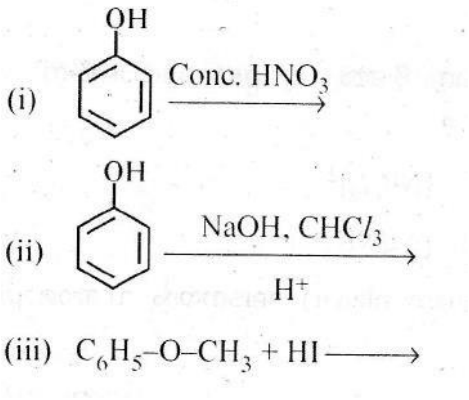


18. a) Identify the product:

$HCHO \xrightarrow{CH_3MgX/H_2O} .....$

i) CH_3OH ii) CH_3CH_2OH iii) $CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3$ iv) $CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2\text{-}CH_3$ (1)

b) Complete the following:



(3) *[SAY 2017]*

Ans: a) $CH_3\text{-}CH_2\text{-}OH$

b) (i) Picric acid OR, 2,4,6-Trinitrophenol OR,

(ii) Salicylaldehyde OR, o-hydroxybenzaldehyde OR,

(iii) $C_6H_5\text{-}OH$ + $CH_3\text{-}I$ [Phenol + Methyl iodide]

19. (a) Grignard reagents are important class of organometallic compounds used to prepare alcohols. Identity the compounds A and B and write the formula.

(i) $HCHO + CH_3MgBr \xrightarrow[(2)\ H_2O]{(1)\ \text{Dry ether}} A + Mg(OH)Br$

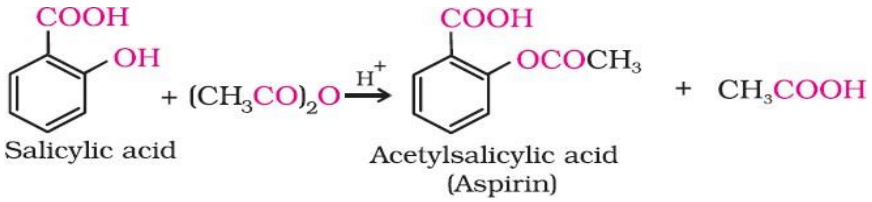
(ii) $B + CH_3MgBr \xrightarrow[(2)\ H_2O]{(1)\ \text{Dry ether}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + Mg(OH)Br$

(b) Write the name of products formed when salicylic acid is treated with acetic anhydride in acid medium. (4) *[March 2018]*

Ans: a) (i) A : CH_3CH_2OH

(ii) B: CH_3-CHO

(b) Acetylsalicylic acid (aspirin) and acetic acid



20. (a) Predict the products A and B.

$3CH_3 - CH = CH_2 + (H-BH_2)_2 \longrightarrow A \xrightarrow{H_2O_2/OH^-} B$

(b) How methanol is prepared industrially? (4) *[SAY 2018]*

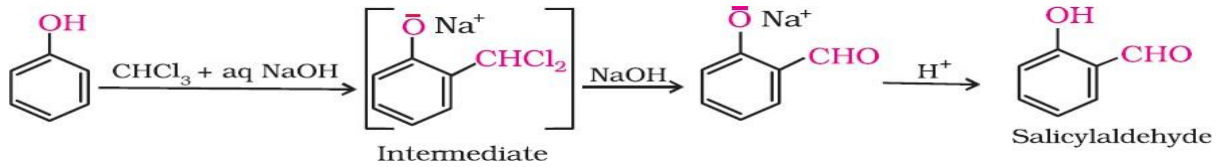
Ans: a) A is triethylborane [$(CH_3-CH_2-CH_2)_3B$] and B is propan-1-ol [$CH_3-CH_2-CH_2-OH$]

b) Methanol is industrially prepared by the catalytic hydrogenation of carbon monoxide at about 573-673 K temperature and 200-300 atm pressure and in the presence of ZnO – Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[200\text{-}300\ \text{atm}\ 573\text{-}673\ K]{ZnO\text{-}Cr_2O_3} CH_3OH$$

21. Write the chemical equation representing Reimer-Tiemann reaction. (2)

Ans: Phenol when treated with chloroform in the presence of sodium hydroxide, followed by acidification, we get salicylaldehyde (o-hydroxybenzaldehyde). This reaction is known as Reimer - Tiemann reaction.



22. Give the structural formula and IUPAC name of the product formed by the reaction of propanone with CH_3MgBr in dry ether, followed by hydrolysis. (2)

Ans: The product formed is $(CH_3)_3C$-OH.

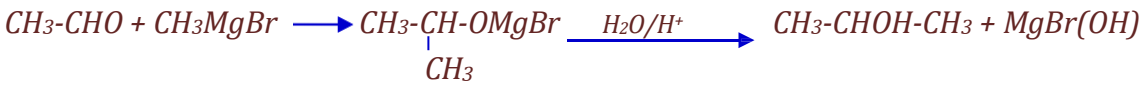
Its IUPAC name is 2-Methylpropan-2-ol

23. Predict the products obtained by the reaction of 2-methoxy-2-methylpropane with HI. (2) *[March 2019]*

Ans: $(CH_3)_3C$-I (tert-butyl iodide or 2-Iodo-2-methylpropane) and CH_3-OH (methyl alcohol or methanol)

24. Write the preparation of propan-2-ol from a Grignard reagent. (2)

Ans: Acetaldehyde (ethanal) reacts with methyl magnesium bromide followed by acidification, we get propan-2-ol.

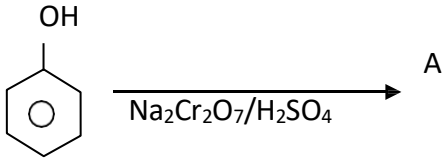


25. Phenols are acidic. Why? (2)

Ans: In phenols, the –OH group is directly bonded to an sp^2 hybridized carbon atom of the benzene ring. Due to the greater electronegativity of sp^2 hybridized carbon, the benzene ring acts as an electron withdrawing group. So it is easy to remove the hydrogen atom as H^+ ion and thus phenol is acidic in nature.

26. (a) What is cumene? Explain the preparation of phenol from cumene. (3)

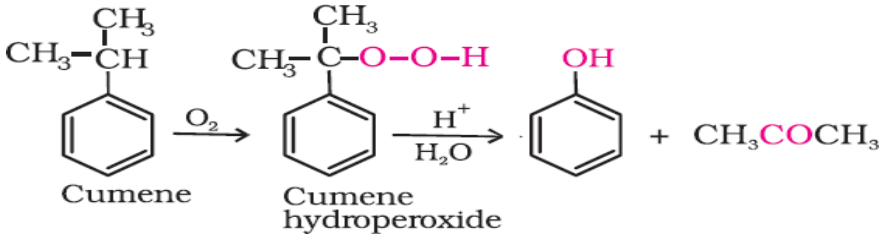
(b) Identify the compound A.



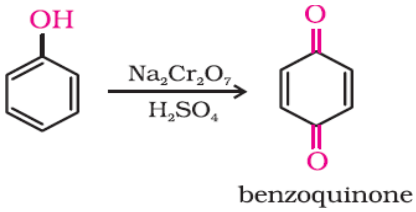
(1) *[SAY 2019]*

Ans: (a) Cumene is isopropylbenzene (2-phenyl propane).

When cumene is oxidised in presence of air followed by hydrolysis in presence of acid, we get phenol.



(b) A is benzoquinone.



27. Ethanol and methoxymethane are functional isomers. But ethanol has higher boiling point than methoxymethane. Give reason. (2)

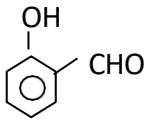
Ans: This is due to the presence of inter molecular hydrogen bonding in ethanol, which is absent in methoxymethane.

28. (a) A mixture of anhydrous $ZnCl_2$ and conc. HCl is an important reagent used to distinguish primary, secondary and tertiary alcohols. How the above reagent is used to distinguish the three types of alcohols? (3)

(b) Predict the product formed in the reaction $CH_3\text{-}CH_2\text{-}OH \xrightarrow[443K]{\text{Conc. } H_2SO_4}$? (1) *[March 2020]*

Ans: (a) Refer the answer of question no. 6 (c)

(b) Ethene ($CH_2=CH_2$)

29. (a) X $\xrightarrow[340\ K]{NaOH + CHCl_3}$  CHO

o – Hydroxybenzaldehyde

Identify X and name the reaction. (2)

(b) How can the following conversions be effected:

(i) Phenol ⟶ Benzene (1)

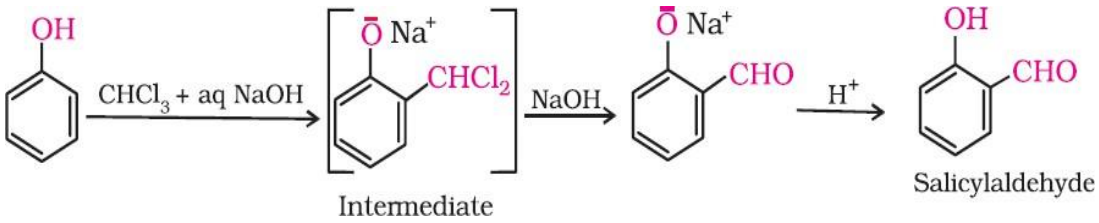
(ii) Phenol ⟶ 2, 4, 6-Trinitrophenol (1) *[SAY 2020]*

Ans: (a) X is phenol (C_6H_5-OH) and the reaction is Reimer-Tiemann reaction.

(b) Refer the answer of question no. 10.

30. Explain the following reactions (i) Reimer-Tiemann reaction (ii) Williamson's synthesis. (3)

Ans: (i) ***Reimer-Tiemann Reaction:*** *Phenol when treated with chloroform in the presence of NaOH, followed by acidification, we get salicylaldehyde (o-hydroxybenzaldehyde).*



(ii) ***Williamson's synthesis:*** *Alkyl halide reacts with sodium alkoxide to form ether. This reaction is called Williamson's ether synthesis.*

$R\text{-}X + R'\text{-}ONa \rightarrow R\text{-}O\text{-}R' + NaX$

31. (i) How are the following conversions carried out?

A. Propene to Propan-2-ol.

B. Ethanal to Ethanol. (2)

(ii) Name the enzyme which converts glucose to ethanol. (1) *[March 2021]*

Ans: (i) A. Propene reacts with water in the presence of acid as catalyst to form propan-2-ol.

$CH_3\text{-}CH{=}CH_2 + H_2O \xrightarrow{H^+} CH_3\text{-}CH(OH)\text{-}CH_3$

B. Ethanal when reduced using lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$) or on catalytic hydrogenation, we get ethanol.

$CH_3\text{-}CHO + [H] \xrightarrow{LiAlH_4} CH_3\text{-}CH_2OH$

(ii) Zymase

32. (i) Which among the following alcohols has the highest boiling point?

(A) CH_3OH (B) $CH_3 – CH_2 – CH_2 – CH_2 – OH$ (C) $CH_3 – CHOH – CH_2 – CH_3$ (D) $CH_3 – CH_2 – CH_2 – OH$ (1)

(ii) Phenol is more acidic than ethanol. Why? (2)

Ans: (i) (B) $CH_3 – CH_2 – CH_2 – CH_2 – OH$

(ii) This is due to the following reasons:

In alcohol, the O-H group is directly bonded to an sp^3 hybridized carbon atom, but in phenol, it is bonded to more electronegative sp^2 hybridized carbon. So the ease of cleavage of O-H bond is greater on phenol and hence it is more acidic than alcohol.

The alkoxide ion ($R\text{-}O^-$) formed by the ionization of alcohol is not resonance stabilized. But the phenoxide ion ($C_6H_5\text{-}O^-$) formed by the ionization of phenol is resonance stabilized. SO phenol readily loses H^+ and hence it is more acidic.

[OR, This is due to the greater electronegativity of sp^2 hybridised carbon atom to which –OH group is attached in phenol and the greater stability of the phenoxide ion formed during the ionisation of phenol.]

33. Explain Lucas test to distinguish primary, secondary and tertiary alcohols. (3) *[SAY 2021]*

Ans: Refer the Answer of the Question number 6 (c).

34. Give a reagent which is used to distinguish 1^0, 2^0 and 3^0 alcohols. (1)

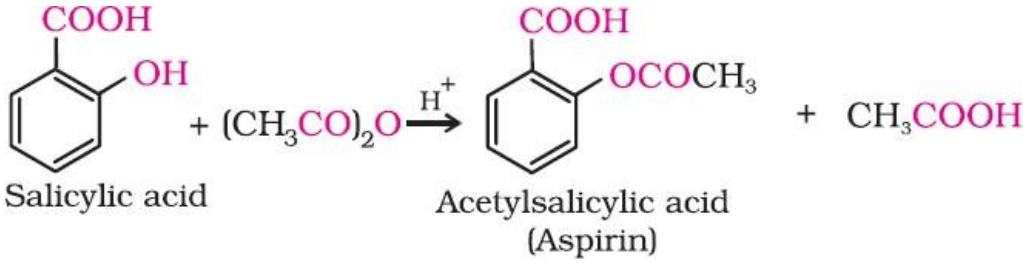
Ans: Lucas reagent (Conc. HCl and anhydrous $ZnCl_2$)

35. (i) Alcohols and phenols have higher boiling points. Why? (1)

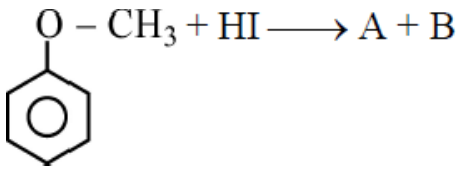
(ii) What is aspirin? How is it prepared from salicylic acid? (2)

Ans: (i) This is due to the inter molecular hydrogen bonding in alcohols and phenols.

(ii) Aspirin is acetyl salicylic acid. It is prepared by the acetylation of salicylic acid.



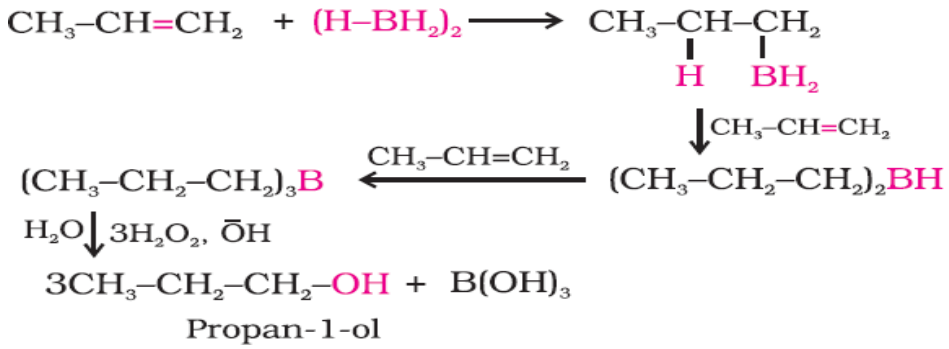
36. (i) Identify A and B in the following reaction (1)



(ii) What is meant by hydroboration - oxidation reaction? Illustrate it with an example. (2) *[March 2022]*

Ans: (i) A is Phenol ($C_6H_5\text{-}OH$) and B is Methyl iodide ($CH_3\text{-}I$)

(ii) Alkenes add diborane to give trialkyl boranes as addition product. This on oxidation by hydrogen peroxide in the presence of aqueous sodium hydroxide to form alcohols. This reaction is known as Hydroboration-oxidation reaction.



37. On heating phenol with chloroform in the presence of NaOH product formed is _____. (1)

Ans: Salicylaldehyde

38. (i) What is "Wood spirit"? (1)

(ii)Explain the commercial preparation of wood spirit. Give the chemical equation. (2)

Ans: (i) Wood spirit is Methanol or Methyl alcohol.

(ii) It is manufactured by the catalytic hydrogenation of carbon monoxide at about 573-673 K temperature and 200-300 atm pressure and in the presence of ZnO – Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[200\text{-}300\ atm,\ 573\text{-}673\ K]{ZnO\text{-}Cr_2O_3} CH_3OH$$

39. Predict A and B

$$HCHO \xrightarrow[2.\ H_2O]{1.\ CH_3CH_2MgBr} A \xrightarrow[[O]]{CrO_3} B$$

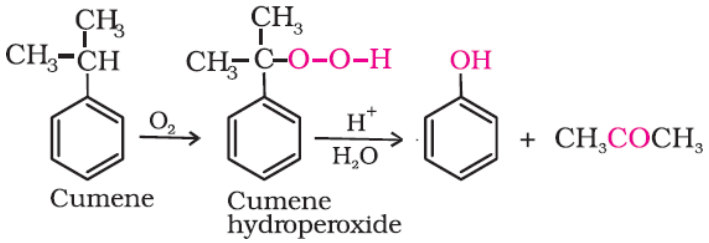
(2) *[SAY 2022]*

Ans: A is $CH_3 – CH_2 – CH_2OH$ (Propan-1-ol or n-Propyl alcohol and

B is $CH_3 – CH_2 – CHO$ [Propanal]

40. How is phenol manufactured industrially ? Write the chemical equation. (2)

Ans: Phenol is manufactured from cumene [isopropylbenzene]. Cumene is oxidised in presence of air followed by acidification gives phenol.



41. Name the products formed when phenol is treated with the following reagents:

(i) Bromine water (1)

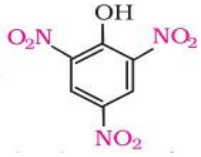
(ii) Zinc dust (1)

(iii) Conc. HNO_3 (1)

Ans:

(i) 2,4,6-Tribromophenol OR, 

(ii) Benzene (C_6H_6) OR, 

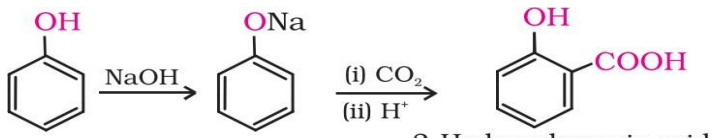
(iii) 2,4,6-Trinitrophenol OR, Picric acid OR, 

42. Explain the following :

(i) Kolbe's reaction (1½)

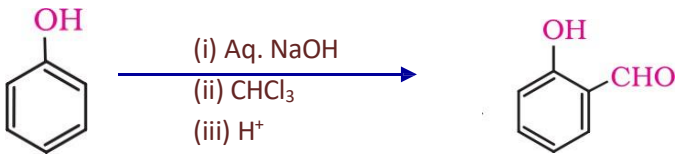
(ii) Reimer-Tiemann reaction (1½) *[March 2023]*

Ans: (i) ***Kolbe's Reaction:*** *When phenol is treated with sodium hydroxide, we get sodium phenoxide, which on treating with CO_2 followed by acidification, we get salicylic acid.*



2-Hydroxybenzoic acid
(Salicylic acid)

(ii) ***Reimer-Tiemann Reaction:*** *When phenol is treated with chloroform in the presence of sodium hydroxide, followed by acidification, we get salicylaldehyde.*



Phenol *Salicylaldehyde*

43. (i) What is the chemical composition of Lucas' Reagent ? (1)

(ii) What is Lucas' Reagent used for ? (1)

Ans: (i) Lucas reagent is a mixture of conc. HCl and anhydrous $ZnCl_2$.

(ii) It is used for the distinction of three types of alcohols.

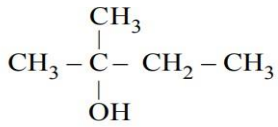
44. Explain the following :

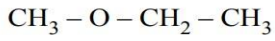
(i) Williamson synthesis (1½)

(ii) Kolbe's Reaction (1½)

Ans: Refer the Answer of the Question number 15 (a) and 42 (i)

45. Write the IUPAC names of the following compounds :

(i)  **(1)**

(ii)  **(1)**

(iii) Alcohols are soluble in water. Give reason. (1) *[SAY 2023]*

Ans: (i) 2-Methylbutan-2-ol

(ii) *Methoxyethane*

(iii) *Due to the formation intermolecular hydrogen bonding with water.*

Aldehydes, Ketones and Carboxylic Acids

1. Aliphatic aldehydes differ from aromatic aldehydes.
   a) Give one example each for an aliphatic aldehyde and an aromatic aldehyde containing seven carbon atoms.
   b) Give one reaction in which the above aldehydes differ. (3) [March 2008]

Ans: (a) Aliphatic aldehyde: CH_3-$(CH_2)_5$-CHO (heptanal)

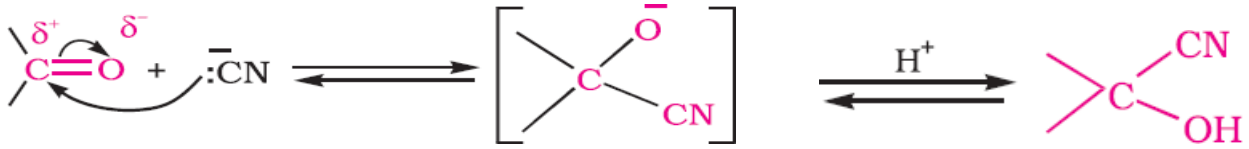
Aromatic aldehyde: C_6H_5-CHO (Benzaldehyde)

(b) When heated with Fehling's solution A and B, heptanal gives a red precipitate, while Benzaldehyde does not.

2. Nucleophilic addition reaction is a characteristic of carbonyl group.
   a) Explain this with specific examples, how the reaction takes place, (2)
   b) i) Show the order of reactivity of following compounds in nucleophilic addition;
   CH_3-CHO, CH_3-CO-CH_3, H-CHO (1)
   ii) Justify your answer. (2) [March 2009]

Ans: (a) The nucleophile attacks the electrophilic sp^2 hybridised carbon atom of the carbonyl group. As a result, the hybridisation of carbon changes from sp^2 to sp^3 and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the product.

E.g. Addition of HCN.



(b) i) The decreasing order of reactivity towards nucleophilic addition reaction is

H-CHO > CH_3-CHO > CH_3-CO-CH_3.

This order is due to the electron releasing effect of CH_3 groups and steric hindrance.

3. a) Show how aldehyde reacts with the following reagents.
   i) $NH_2CONHNH_2$ (Semi carbazide)
   ii) Zinc amalgam and conc. HCl (2)
   b) i) How can you manufacture formic acid from CO? (1)
   ii) Suggest a chemical test to distinguish this acid from acetic acid. Account for the observation. (2)
   [March 2009]

Ans: a) (i) Aldehydes react with semicarbazide to form semicarbazone.

R-CHO + NH_2-NH-CO-NH_2 → R-CH=N-NH-CO-NH_2 + H_2O

(semicarbazone)

(ii) Aldehydes when treated with zinc amalgam and concentrated hydrochloric acid to form alkanes.

CH_3-CHO + [H] $\xrightarrow{Zn/Hg}$ CH_3-CH_3

b) i) Carbon monoxide reacts with aq. NaOH to form sodium formate, this on acidification with dil. H_2SO_4 to form formic acid.

CO + NaOH $\xrightarrow{H_2O}$ HCOONa $\xrightarrow{H_2SO_4}$ HCOOH

ii) Iodoform test. When acetic acid is treated with sodium hypoiodite (NaOI), we get an yellow ppt of iodoform. This reaction is not answered by formic acid.

4. a) Aldehydes and ketones are organic compounds containing carbonyl group.

i) Write a chemical reaction used to distinguish between aldehydes and ketones. (1)

ii) Aldehydes and ketones can be subjected to Clemmensen reduction and Wolff-Kishner reduction. Name the reagents in both cases. (1)

b) How will you make the following conversions:

i) Ethanoic acid to ethanol.

ii) Propanoic acid to 2-chloropropanoic acid

iii) Toluene to benzoic acid. (3) [March 2010]

Ans: (a) i) Tollen's test or Fehling's test

ii) Clemmensen reduction: Zinc amalgam and Conc. HCl

Wolff-Kishner reduction: Hydrazine & KOH in ethylene glycol.

(b) i) By reduction using $LiAlH_4$ followed by acidification, ethanoic acid gets converted to ethanol.

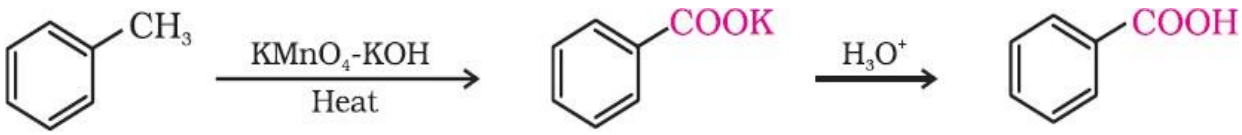
$$CH_3\text{-}COOH \xrightarrow{i)\ LiAlH_4/ether\ or\ B_2H_6\ ii)\ H_3O^+} CH_3\text{-}CH_2OH$$

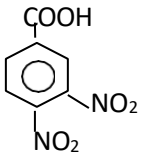
ii) When treated with chlorine in the presence of red phosphorus propanoic acid gets converted to 2-chloropropanoic acid.

$$CH_3\text{-}CH_2\text{-}COOH \xrightarrow{i)\ Cl_2/\ Red\ P\ ii)\ H_2O} CH_3\text{-}CHCl\text{-}COOH + HCl$$

Propanoic acid *2-chloropropanoic acid*

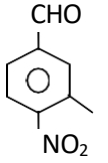
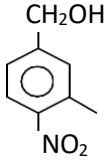
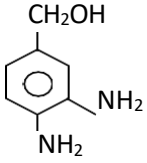
iii) Toluene when heated with alkaline $KMnO_4$ followed by acidification, we get benzoic acid.



5.  is an aromatic acid

a) What is its IUPAC name? (½)

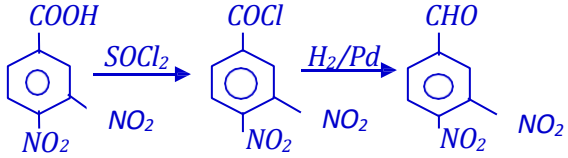
b) Explain the conversion of the above acid to the following:

i)  ii)  iii) 

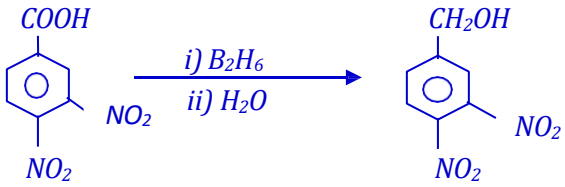
(4½) [March 2011]

Ans: (a) 3,4-Dinitrobenzoic acid

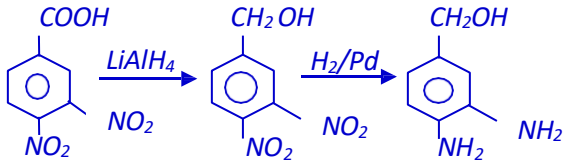
(b) i) 3,4 –dinitrobenzoic acid is treated with thionyl chloride ($SOCl_2$) followed by treating with H_2 in presence of Pd supported over $BaSO_4$ (Rosenmund's reduction) we get 3,4-dinitrobenzaldehyde.



ii) 3,4 –dinitrobenzoic acid is reduced with diborane or $LiAlH_4$ followed by hydrolysis, we get 3,4-dinitrobenzyl alcohol.



iii) 3,4 –dinitrobenzoic acid is treated with $LiAlH_4$ followed by reduction with H_2 in presence of Pd (or, by Fe and HCl or Sn and HCl), we get 3,4-diaminobenzyl alcohol.



6. Aldehydes resemble ketones in many respects.
   a) Give the reason for their resemblance. (1)
   b) Give a reaction in which aldehydes resemble ketones. (1)
   c) Write two tests to distinguish between aldehydes and ketones. (2)
   d) What is Cannizzaro reaction? (1) [SAY 2011]

Ans: a) Because of the presence of carbonyl group in both aldehyde and ketones.

b) Both aldehydes and ketones undergo nucleophilic addition reaction with HCN and form cyanohydrins.

c) Aldehydes form bright silver mirror when heated with Tollens' reagent (Tollens' test). When heated with Fehling's solutions, aldehydes form red ppt of cuprous oxide (Fehling's test). These two tests are not answered by ketones.

d) Aldehydes having no α-hydrogen atom, when treated with conc. KOH undergo self oxidation and reduction (disproportionation) to form alcohol and carboxylic acid salt. This reaction is called Cannizzaro reaction.

$$2\,HCHO \xrightarrow{Conc.\ KOH} CH_3\text{-}OH + H\text{-}COOK$$

Formaldehyde methanol potassium formate

7. a) Which name reaction is used to reduce CH_3-CO-Cl to CH_3-CHO? (1)
   b) Aldehydes and ketones undergo reactions due to the presence of α-hydrogen atom.
   i) Write the name reaction of aldehyde which takes place only because of the presence of α-hydrogen atom. (1)
   ii) How will you bring about the above reaction? (1)
   c) i) CH_2Cl-COOH is a strong acid than CH_3COOH. Why?
   ii) How will you convert CH_3-COOH to CH_2Cl-COOH? (2) [March 2012]

Ans: (a) Rosenmund's reduction

b) i) Aldol condensation

ii) By treating with dilute alkali (NaOH or KOH).

c) i) Due to the electron withdrawing inductive effect (-I effect) of Chlorine atom.

ii) By treating with Cl_2 in presence of red phosphorus (HVZ reaction).

8. a) Complete the following: Write down the structures of A, B and C.

i) $CH_3\text{-}CH_2\text{-}CHO \xrightarrow{KMnO_4} A$

ii) $CH_3\text{-}CH_2\text{-}CO\text{-}CH_3 \xrightarrow{Zn\ amalgam/Conc.HCl} B$

iii) $CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH \xrightarrow{(i)\ Bromine/Red\ P\ (ii)\ H_2O} C$

b) Write down the IUPAC names of A, B and C. (1½)

c) Explain the following reactions: i) Cannizzaro reaction. ii) Esterification. (1) [SAY 2012]

Ans: (a)

i) $CH_3\text{-}CH_2\text{-}CHO \xrightarrow{KMnO_4} CH_3\text{-}CH_2\text{-}COOH$

ii) $CH_3\text{-}CH_2\text{-}CO\text{-}CH_3 \xrightarrow{Zn\ amalgam/Conc.HCl} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

iii) $CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH \xrightarrow{(i)\ Bromine/Red\ P\ (ii)\ H_2O} CH_3\text{-}CH_2\text{-}CHBr\text{-}COOH$

(b) IUPAC name of A is propanoic acid, B is butane and C is 2-Bromobutanoic acid.

(c) i) Cannizzaro reaction: Aldehydes having no α-hydrogen atom, when treated with conc. KOH undergo self-oxidation and reduction (disproportionation) to form alcohol and carboxylic acid salt.

$$2\ HCHO \xrightarrow{Conc.\ KOH} CH_3\text{-}OH + H\text{-}COOK$$

ii) Esterification: Carboxylic acids when heated with alcohols or phenols in the presence of conc. H_2SO_4 or HCl gas, we get esters.

$$R\text{-}COOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} R\text{-}COOR' + H_2O$$

9. a) Suggest a method of preparation of benzaldehyde from toluene. (1)

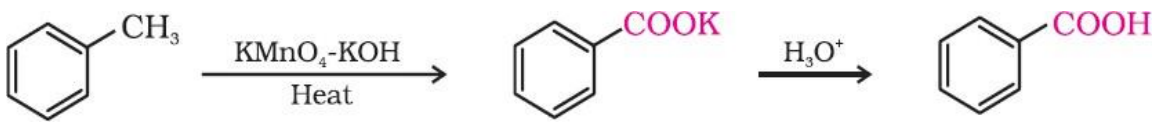
b) Aldehydes and ketones differ in their chemical reactions. How do they react with the following?

i) Tollens' reagent ii) Alcohol. (2)

c) How will you convert propanoic acid into the following compounds?

i) Ethane ii) Butane. (2) [March 2013]

Ans: (a)



(b) i) With Tollens' reagent, aldehydes form bright silver mirror.

ii) With alcohols, aldehydes form hemi-acetals and acetals.

c) i) When propanoic acid is treated with NaOH, we get sodium propanoate. This on heating with soda lime, we get ethane. [Decarboxylation reaction]

$$CH_3\text{-}CH_2\text{-}COONa + NaOH \xrightarrow{CaO/\Delta} CH_3\text{-}CH_3 + Na_2CO_3$$

ii) When propanoic acid is treated with NaOH or KOH, followed by electrolysis, we get butane (Kolbe's Electrolysis).

$$2\ CH_3\text{-}CH_2\text{-}COOK + 2\ H_2O \xrightarrow{Electrolysis} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 2KOH + H_2 + 2CO_2$$

10. a) Among formaldehyde, acetaldehyde and formic acid, which compounds undergo Cannizzaro reaction? Give reason. (1½)

b) What is esterification? (1)

c) Thionyl chloride is preferred to as the reagent to prepare acid chlorides. Why? (½)

d) Write the chemical reaction to effect the transformation of sodium acetate to ethane. (1)

e) Write the IUPAC names of the compounds given below.

i) $CH_3\text{-}CH_2\text{-}CO\text{-}CH_3$ ii) $HOOC\text{-}CH_2\text{-}COOH$. (1) [SAY 2013]

Ans: (a) Formaldehyde. In formaldehyde, there is no α-H atom. So it can undergo Cannizzaro reaction.

(b) Carboxylic acids when heated with alcohols or phenols in the presence of conc. H_2SO_4 or HCl gas, we get esters.

(c) When thionyl chloride is used, the acid chloride formed is pure.

(d) $2\,CH_3\text{-}COONa + 2\,H_2O \xrightarrow{Electrolysis} CH_3\text{-}CH_3 + 2KOH + H_2 + 2CO_2$ [Kolbe's electrolysis]

(e) i) Butanone ii) Propane-1,3-dioic acid

11. a) Aldol condensation reaction is a special reaction of aldehydes.
    i) What is aldol condensation reaction? (1)
    ii) Write the structural formula of aldol formed from ethanal (1)
    b) Write simple chemical tests and observations used to distinguish between the following compounds:
    i) Propanal and propanone (1)
    ii) Phenol and benzoic acid (1)
    c) Write the names of the reagents used to bring about the following transformations
    i) $C_6H_5COCl \longrightarrow C_6H_5CHO$
    ii) $CH_3COOH \longrightarrow CH_2Cl\text{-}COOH$ (1) [March 2014]

Ans: (a) (i) Aldehydes having at least one α-hydrogen atom when heated with dilute alkali, we get α,β-unsaturated aldehyde. This reaction is called Aldol condensation.

$2CH_3\text{-}CHO \xrightleftharpoons{dil.\ NaOH} CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO \longrightarrow CH_3\text{-}CH{=}CH\text{-}CHO$

Ethanal 3-Hydroxybutanal (aldol) But-2-enal (Crotanaldehyde)

(ii) $CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2\text{-}CHO$

(b) i) Tollens' test. When heated with Tollens' reagent propanal gives a bright silver mirror.

ii) Reaction with $NaHCO_3$. Benzoic acid gives brisk effervescence of CO_2 on treating with $NaHCO_3$.

(c) i) H_2 in presence of Pd supported on $BaSO_4$. [Rosenmund's reduction]

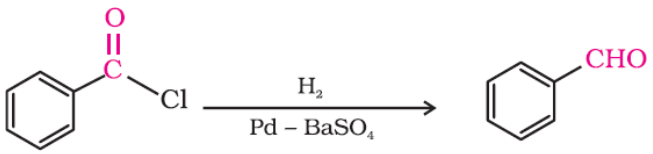
ii) Cl_2 in presence of red P [HVZ Reaction]

12. a) Methanal (HCHO) is an aldehyde having no α-hydrogen atom. What are the products formed when methanal is treated with strong KOH solution? (1)
    b) How are the following conversions achieved?
    i) Benzoyl chloride (C_6H_5COCl) to benzaldehyde ($C_6H_5\text{-}CHO$)
    ii) Acetic acid (CH_3COOH) to chloroacetic acid ($CH_2Cl\text{-}COOH$)
    iii) Benzene to Benzaldehyde
    iv) Ethanal ($CH_3\text{-}CHO$) to Ethane ($CH_3\text{-}CH_3$) (1 X 4 = 4) [SAY 2014]

Ans: (a) Methanol ($CH_3\text{-}OH$) and potassium formate (HCOOK)

$2\,HCHO \xrightarrow{Conc.\ KOH} CH_3\text{-}OH + H\text{-}COOK$

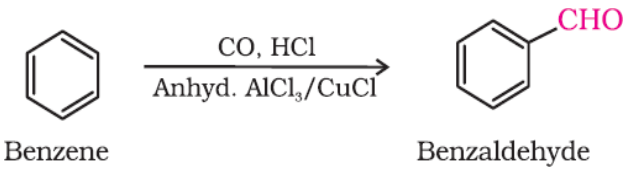
(b) i) Rosenmund's reduction:



ii) HVZ Reaction:

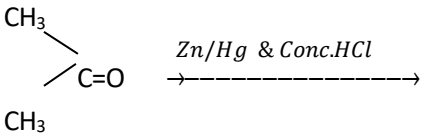
$CH_3\text{-}COOH \xrightarrow{(i)\ Chlorine/Red\ P\ (ii)\ H_2O} CH_2Cl\text{-}COOH + HCl$

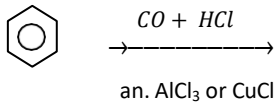
iii) Gattermann – Koch reaction:



iv) Clemmensen reduction: $CH_3\text{-}CHO + [H] \xrightarrow{Zn\ amalgam/Conc.HCl} CH_3CH_3$

13. Aldehydes, Ketones and Acids contain >C=O group.
    a) Name the product obtained by the reaction between acetic acid and ethanol. (1)
    b) (i) Give any two tests to distinguish between aldehydes and ketones. (2)
    (ii) Two chemical reactions are given below:
        (1) Identify the products of each reaction.
        (2) Give the name of each reaction.





(2) [March 2015]

Ans: (a) Ethyl acetate or ethyl ethanoate [$CH_3\text{-}COOC_2H_5$]

(b) (i) Tollens' test and Fehling's test

(ii) (1) Propane [$CH_3\text{-}CH_2\text{-}CH_3$]

Benzaldehyde [$C_6H_5\text{-}CHO$]

(2) Clemmensen reduction and Gattermann-Koch Reaction

14. a) Explain aldol condensation taking CH_3-CHO as example. (2)
    b) Write the named reactions involved in the following conversions:
    i) $CH_3\text{-}CO\text{-}Cl \xrightarrow{H_2/Pd - BaSO_4} CH_3\text{-}CHO$
    ii) $2\ HCHO \xrightarrow{Conc.\ NaOH} HCOONa + CH_3\text{-}OH$ (1)
    c) How are the following conversions achieved?
    i) $CH_3\text{-}CN \longrightarrow CH_3\text{-}COOH$
    ii) $CH_3\text{-}COOH \longrightarrow CH_2Cl\text{-}COOH$ (2) [SAY 2015]

Ans: (a) Refer the answer of Question no. 11 (a)

(b) i) Rosenmund's reduction

ii) Cannizzaro's reaction

(c) i) $CH_3\text{-}CN \xrightarrow{H_2O/H^+} CH_3\text{-}COOH$

ii) $CH_3\text{-}COOH \xrightarrow{(i)\ Chlorine/Red\ P\ (ii)\ H_2O} CH_2Cl\text{-}COOH$

15. Aldehydes, Ketones and Carboxylic acids are Carbonyl compounds.
    a) Aldehydes differ from Ketones in their oxidation reactions. Illustrate with one example. (1)
    b) How will you prepare benzaldehyde by Gatterman-Koch reaction? (1)

c) Write the reactions of carboxylic acid with the following reagents. (Write the chemical equations)

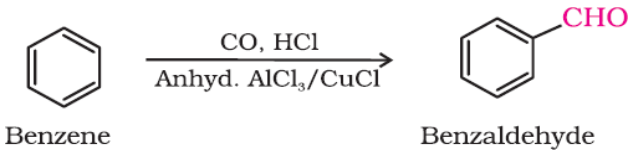
(i) Thionyl chloride ($SOCl_2$)

(ii) Chlorine in presence of small amount of red phosphorous.

(iii) Lithium Aluminium hydride ($LiAlH_4$)/ether. (3)

Ans: (a) Aldehydes readily undergo oxidation and form carboxylic acid. Ketones when oxidised using strong oxidising agent undergo C-C bond cleavage and form a mixture of carboxylic acids.

(b) Benzene when treated with CO and HCl in the presence of anhydrous aluminium chloride or cuprous chloride, we get benzaldehyde.



(c) (i) $R\text{-}COOH + SOCl_2 \rightarrow R\text{-}COCl + SO_2 + HCl$

(ii) $R\text{-}CH_2\text{-}COOH \xrightarrow{(i)\ Chlorine/Red\ P\ (ii)\ H_2O} R\text{-}CHCl\text{-}COOH$

(iii) $R\text{-}COOH \xrightarrow{LiAlH_4/ether} R\text{-}CH_2\text{-}OH$

16. a) Write a test to distinguish between aldehydes and ketones. (1)

b) How will you prepare benzaldehyde by Etard's reaction? (1)

c) How will you bring about the following conversions? (Write the chemical equations)

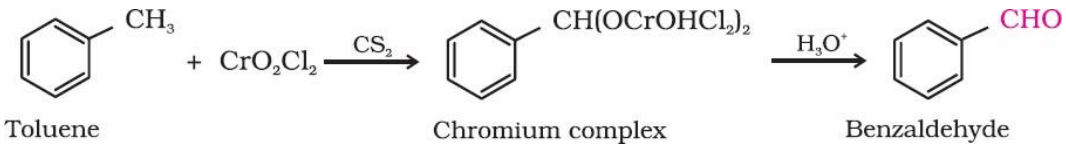
(i) Ethanol → Ethanoic acid

(ii) Benzamide → benzoic acid

(iii) Benzaldehyde → meta nitrobenzaldehyde (3) [March 2016]

Ans: (a) Tollens' test

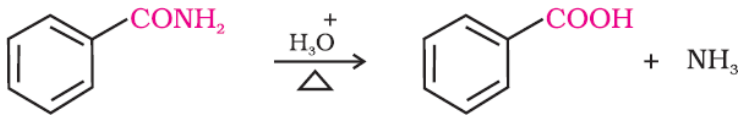
*(b) When toluene is oxidised using chromyl chloride (CrO_2Cl_2) in CS_2 followed by hydrolysis (acidification), we get benzaldehyde. This reaction is called **Etard reaction**.*



(c) (i) $CH_3\text{-}CH_2\text{-}OH \xrightarrow{K_2Cr_2O_7/H^+} CH_3\text{-}COOH$

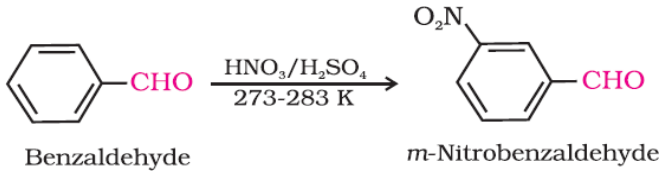
ethanol ethanoic acid

ii)



Benzamide Benzoic acid

iii)



17. Aldehydes and ketones are the compounds having >C = O group.

a) Choose the IUPAC name of the compound CH_3-CH = CH-CHO

(i) Propen-1-al (ii) But-2-en-1-al (iii) Butanal (iv) But-2-en-2-al (1)

b) Complete the following reactions:

(i) $HCHO + conc.\ KOH \xrightarrow{\Delta}$

(ii) $CH_3\text{-}CHO \xrightarrow{dil.\ NaOH}$

(iii) $CH_3\text{-}CHO + H_2N\text{-}NH_2 \rightarrow$

(iv) $C_6H_5COCH_3 \xrightarrow{Zn/Hg\ \&\ conc.HCl}$ (4)

Ans: (a) But-2-en-1-al

(b)

(i) $HCHO + conc.\ KOH \xrightarrow{\Delta} CH_3\text{-}OH + HCOOK$

(ii) $CH_3\text{-}CHO \xrightarrow{dil.\ NaOH} CH_3\text{-}CHOH\text{-}CH_2\text{-}CH_3$

(iii) $CH_3\text{-}CHO + H_2N\text{-}NH_2 \rightarrow CH_3\text{-}CH{=}N\text{-}NH_2$

(iv) $C_6H_5COCH_3 \xrightarrow{Zn/Hg\ \&\ conc.HCl} C_6H_5CH_2CH_3$

18. Aldehydes, ketones and acids contain >C = O group.

a) Choose the IUPAC name of the compound $(CH_3)_2$CH-COOH.

(i) Butanoic acid (ii) Ethanoic acid (iii) 2-Methylpropanoic acid (iv) Propanoic acid (1)

b) Complete the following reactions:

(i) $CH_3\text{-}CH_2\text{-}COOH \xrightarrow{LiAlH_4/ether}$

(ii) $CH_3\text{-}CH_2\text{-}COOH + SOCl_2 \rightarrow$

(iii) $CH_3\text{-}CH_2\text{-}COOH \xrightarrow{Bromine/Red\ P}$

(iv) $CH_3\text{-}CH_2\text{-}COOH + CH_3\text{-}OH \xrightleftharpoons{H^+}$ (4) [SAY 2016]

Ans: (a) 2-Methylpropanoic acid

(b) (i) $CH_3\text{-}CH_2\text{-}COOH \xrightarrow{LiAlH_4/ether} CH_3\text{-}CH_2\text{-}CH_2OH$

(ii) $CH_3\text{-}CH_2\text{-}COOH + SOCl_2 \rightarrow CH_3\text{-}CH_2\text{-}COCl$

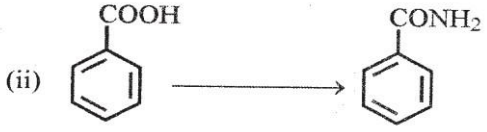
(iii) $CH_3\text{-}CH_2\text{-}COOH \xrightarrow{Bromine/Red\ P} CH_3\text{-}CHBr\text{-}COOH$

(iv) $CH_3\text{-}CH_2\text{-}COOH + CH_3\text{-}OH \xrightleftharpoons{H^+} CH_3\text{-}CH_2\text{-}COOCH_3$

19. a) The product obtained when benzene is treated with carbon monoxide and hydrogen chloride in presence of anhydrous $AlCl_3$ is: i) Chlorobenzene ii) Phenol iii) Benzaldehyde iv) Benzoic acid (1)

b) How will you carry out the following conversions?

(i) 

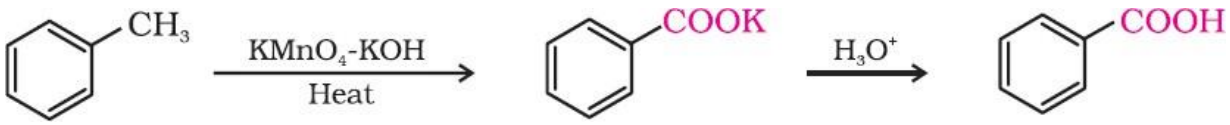
(ii) 

(iii) $CH_3\text{-}CH_2\text{-}COOH \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$

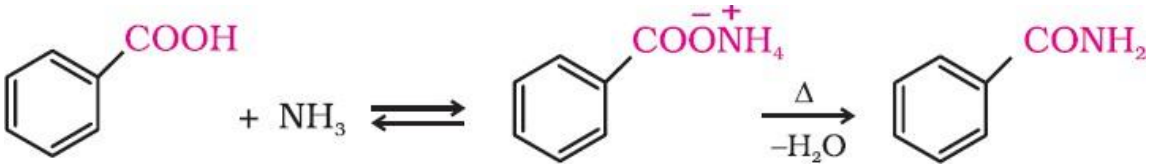
(IV) CH_3-COOH $\longrightarrow$ CH_3-CO-O-CO-CH_3 (acetic anhydride) (4) [March 2017]

Ans: (a) (iii) Benzaldehyde

(b) (i) Toluene when heated with alkaline $KMnO_4$ followed by acidification, we get benzoic acid.



(ii) Benzoic acid when heated with NH_3, we get benzamide.



(iii) Propanoic acid when reduced using $LiAlH_4$, we get 1-propanol.

$$CH_3\text{-}CH_2\text{-}COOH \xrightarrow{LiAlH_4/ether} CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$$

(iv) Acetic acid when heated with Conc. H_2SO_4 or P_2O_5, we get acetic anhydride.

$$CH_3\text{-}COOH \xrightarrow{Conc.\ H_2SO_4/\Delta} CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3$$

20. Explain the following:

i) Esterification ii) Tollen's test iii) HVZ reaction iv) Decarboxylation of carboxylic acid (4) [March 2017]

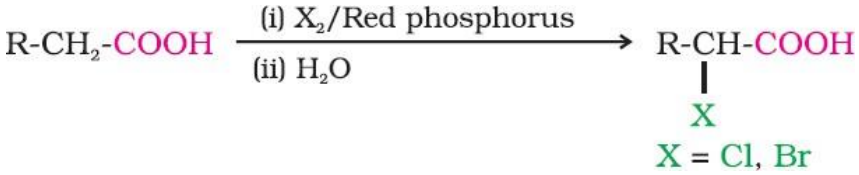
*Ans: (i) **Esterification**: Carboxylic acids when heated with alcohols or phenols in the presence of a mineral acid like concentrated H_2SO_4 or HCl gas, we get esters. Or the equation:*

$$R\text{-}COOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} R\text{-}COOR' + H_2O$$

*(ii) **Tollen's test:** When an aldehyde is heated with Tollens' reagent, we get a bright silver mirror. Or the equation:*

$$R\text{-}CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow R\text{-}COO^- + 2\,Ag + 2\,H_2O + 4\,NH_3$$

*(iii) **HVZ reaction**: Carboxylic acids having an α-hydrogen atom, when treated with halogen (chlorine or bromine) in the presence of red phosphorus, we get α-halocarboxylic acids. This reaction is known as Hell-Volhard-Zelinsky(HVZ) reaction. Or the equation:*



*(iv) **Decarboxylation of carboxylic acid**: When sodium salt of carboxylic acid is heated with sodalime (a mixture of NaOH and CaO), we get alkanes. Or the equation:*

$$R\text{-}COONa + NaOH \xrightarrow{CaO/\Delta} R\text{-}H + Na_2CO_3$$

21. a) Which among the following reduces Tollen's reagent?

i) Methanal ii) Propanone iii) Benzophenone iv) Acetophenone (1)

b) Since both aldehydes and ketones possess carbonyl functional group, they undergo similar chemical reactions.

i) Explain the structure of carbonyl group. (2)

ii) Explain aldol condensation with an example. (2) [SAY 2017]

Ans: (a)Methanal

(b) i) The carbonyl carbon atom is sp^2-hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon forms a π-bond with oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π-electron cloud is above and below this plane.

ii) Refer the answer of the question no. 11 (a)

22. a) Which among the following does not give red precipitate with Fehling's solution?

i) Ethanal ii) Propanal iii) Butanal iv) Benzaldehyde (1)

b) How will you bring about the following conversions?

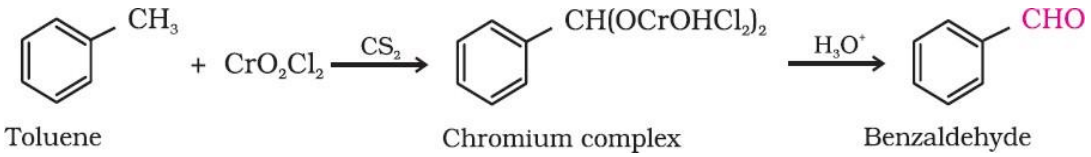
i) Toluene to Benzaldehyde

ii) Benzoic acid to Benzamide (2)

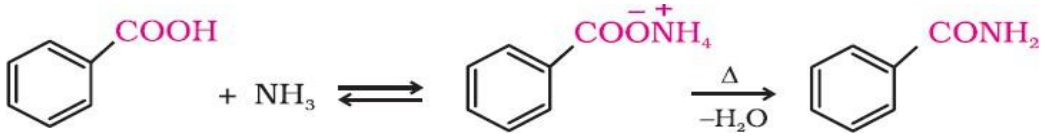
c) Explain Cannizaro reaction with an example. (2)

Ans: (a) Benzaldehyde

(b) i) By Etard's reaction



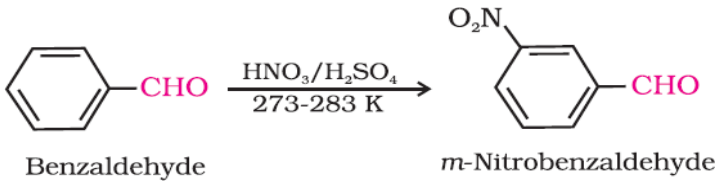
ii) *Benzoic acid reacts with NH_3 to form ammonium benzoate which on heating to form benzamide.*



c) *Refer the answer of the question no. 6 (d)*

23. Aromatic aldehydes undergo electrophilic substitution reactions. Write the nitration reaction of benzaldehyde with chemical equation. (2)

Ans:



24. Briefly describe Gattermann Koch reaction. (2)

Ans: Refer the answer of the question no. 12 (b)

25. How would you account for the followings :

a) Aldehydes are more reactive than ketones towards nucleophilic addition reaction.

b) Boiling point of aldehydes is lower than alcohols.

c) Addition reaction of sodium hydrogen sulphite is useful for the separation and purification of aldehydes.

(3x1 =3) [March 2018]

Ans: (a) Due to electronic effect and steric effect.

(b) Due to the absence of intermolecular hydrogen bonding in aldehydes.

(c) Since the product obtained is water soluble and can be converted back to the original aldehyde by treating with dil. acid or alkali.

26. Identify A and B in the following equations :

(a) $H-CHO + H-CHO \xrightarrow[\Delta]{\text{Con. KOH}} A + B$

(b) $2\,CH_3-CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} A \xrightarrow[-H_2O]{\Delta} B$ (2)

Ans: (a) A is CH_3-OH and B is HCOOK

(b) A is CH_3-CHOH-CH_2-CH_3 and B is CH_3-CH=CH-CH_3

27. How the conversion of carbon dioxide to carboxylic acid can be effected using Grignard reagent? (2)

Ans: CO_2 reacts with Grignard reagent in dry ether followed by hydrolysis, we get carboxylic acid.

$$R\text{-}Mg\text{-}X + O{=}C{=}O \xrightarrow{\text{Dry ether}} R-C(=O)-O^-MgX^+ \xrightarrow{H_3O^+} RCOOH$$

28. How the conversion of an aldehyde to acetal can carry out? (Write chemical equations) (3) [SAY 2018]

Ans: Aldehyde reacts with alcohol in the presence of dry HCl to give hemiacetal (alkoxyalcohol), which further react with one molecule of alcohol to give a gem-dialkoxy compound known as acetal.

$$R{-}CHO \underset{}{\overset{R'OH,\ HCl\ gas}{\rightleftharpoons}} \underbrace{R{-}CH(OR')(OH)}_{\text{Hemiacetal}} \underset{H^+}{\overset{R'OH}{\rightleftharpoons}} \underbrace{R{-}CH(OR')_2}_{\text{Acetal}} + H_2O$$

29. Identify the products and give the name of the following reaction :

$$C_6H_5CHO \xrightarrow[Conc.\ NaOH/\Delta]{} \text{Products}$$ (2)

$$C_6H_5CHO \xrightarrow[Conc.\ NaOH/\Delta]{} C_6H_5CH_2OH + C_6H_5COONa$$

The reaction is known as Cannizzaro reaction.

30. Explain Haloform reaction. (2)

Ans: Compounds having CH_3-CO- group or CH_3-CHOH- group, when treated with sodium hypohalite or halogen in presence of NaOH, we get a haloform (CHX_3). This reaction is called haloform reaction.

$$R\text{-}CO\text{-}CH_3 \xrightarrow{NaOX\ Or\ X_2\ \&\ NaOH} R\text{-}COONa + CHX_3 \text{ (where X = Cl, Br or I)}$$

31. Identify A, B and C in the following sequence of reactions :

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^-NH_4^+ \xrightarrow{\Delta} A \xrightarrow{H_3O^+} B \xrightarrow{Br_2/Red\ P} C$$ (3) [March 2019]

Ans: A = CH_3-$CONH_2$, B = CH_3-COOH and C= CH_2Br-COOH

32. Describe the following with equations : (a) Etard reaction (b) Aldol condensation (4) [SAY 2019]

Ans: Refer the answer of the question numbers 11 (a) and 16 (b)

33. Among the following which is more acidic? (a) HCOOH b) CH_3CH_2COOH (c) CH_3COOH (d) $CH_3CH_2CH_2COOH$ (1)

Ans: HCOOH

34. Give a chemical test to distinguish between propanal and propanone. (2)

Ans: Propanal (being an aldehyde) gives the following tests:

*i) **Tollen's test**: When heated with Tollen's reagent, Propanal gives a bright silver mirror*

*ii) **Fehling's test**: When heated with equal volume of Fehling's solutions A and B, Propanal gives reddish brown ppt.*

iii) ***Schiff's test****: Propanal restore the pink colour of Schiff's reagent.*

The above tests are not answered by propanone (being a ketone).

Iodoform (Haloform) Test*: Propanone gives an yellow ppt, when treated with sodium hypoiodite or I_2 in presence of NaOH. Propanal does not give this test.* [***Only one test is required***]

35. Explain the following reactions: (a) Rosenmund reduction (b) Cannizzaro reaction. (2 x 2 = 4) [March 2020]

Ans: (a) Rosenmund reduction : Acid chlorides react with hydrogen in presence of Pd supported on $BaSO_4$, we get aldehydes. This reaction is called Rosenmund's reduction.

$$R\text{-}COCl + H_2 \xrightarrow{Pd/BaSO_4} R\text{-}CHO + HCl$$

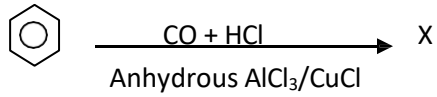
(b) Refer the answer of the question numbers 6 (d)

36. In Etard reaction, benzaldehyde can be prepared by the oxidation of toluene by _____.

(a) $KMnO_4$ (b) $K_2Cr_2O_7$ (c) CrO_2Cl_2 (d) CrO_3 (1)

Ans: CrO_2Cl_2

37.



(a) Identify the Product X (1)

(b) Name the reaction. (1)

Ans: (a) Benzaldehyde [C_6H_5-CHO]

(b) Gattermann Koch reaction

38. (a) Give a chemical test to distinguish aldehydes from ketones. (1)

(b) Carbonyl group (>CO) of aldehydes and ketones can be reduced to CH_2 group in Clemmensen reduction. Name the reagent used. (1)

Ans: (a) Tollens' test

(b) Zinc amalgam and Conc. HCl.

39. With the help of chemical reaction explain the following name reactions:

(a) Aldol condensation (b) HVZ reaction (2 x 2 = 4) [SAY 2020]

Ans: (a) Refer the answer of the question no. 11 (a)

(b) Refer the answer of the question no. 20 (iii)

40. (i) The test to distinguish Propanal and Propanone is .....

(A) Tollens' test (B) Lucas test (C) Hinsberg test (D) Bromine-Water test (1)

(ii) Which is more reactive towards nucleophilic addition, CH_3CHO or C_6H_5-CHO? Give reason. (2)

Ans: (i) Tollens' test

(ii) CH_3-CHO

C_6H_5-CHO (Benzaldehyde) is less reactive because of the less electrophilicity of the carbonyl carbon due to resonance. ***Or****, due to the presence of bulky phenyl group (steric hindrance).*

41. Identify the products and name the reactions.

(i) HCHO $\xrightarrow{Conc.\ KOH}$ ..... (1)

(ii) CH_3CHO $\xrightarrow{dil.\ NaOH}$ ..... (1)

Ans: (i) CH_3-OH (methanol) and H-COOK (Potassium formate)

(ii) CH_3-CH(OH)-CH_2-CHO (3-Hydroxybutanal)

42. (i) How will you prepare Benzaldehyde from the following:

A. Toluene

B. Benzene

C. Benzoyl chloride (3)

(ii) Identify the product obtained when Acetic acid is heated with P_2O_5. (1) [March 2021]

Ans: (i) Refer the answer of the question no. 12 (b) and 22 (b)

(ii) Ethanoic anhydride or acetic anhydride or $(CH_3\text{-}CO)_2O$

43. A compound is converted into '2-Chloropropanoic acid' by HVZ reaction. Identify the compound and the reagent used. (2)

Ans: $CH_3\text{-}CH_2\text{-}COOH$ (Propanoic acid).

Reagent used is Cl_2 in presence of Red Phosphorus.

44. (i) Write the IUPAC name of CH_3CHO. (1)

(ii) Give two methods for the conversion R-CN into R-CHO. (2)

(iii) Identify the class of product formed when HCN is added to an aldehyde or ketone. (1)

Ans: (i) Ethanal

*(ii) (a) By reduction using stannous chloride ($SnCl_2$) in the presence of hydrochloric acid followed by acidification [**Stephen reaction**]*

(b) By reduction using diisobutylaluminium hydride (DIBAL-H) to imines followed by hydrolysis.

(iii) Cyanohydrin

45. Explain the following :

(i) Tollens' reagent test. (2)

(ii) Gatterman-Koch reaction. (2) [SAY 2021]

Ans: (i) Refer the Answer of Question number 6 (c)

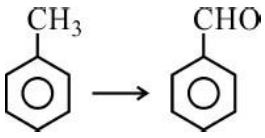
(ii) Refer the Answer of Question number 15 (b)

46. (i) Write the products of the following reaction : (2)

$$2H - CHO \xrightarrow[\Delta]{\text{Con NaOH}} \_\_\_\_\_ + \_\_\_\_\_$$

(ii) Explain Hell – Volhard – Zelinsky (HVZ) reaction. (2)

(iii) Suggest a suitable method for the following conversion : (2)

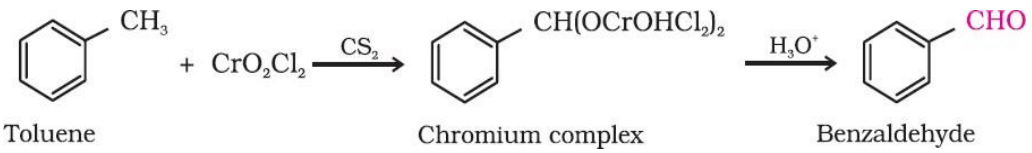


[March 2022]

Ans: (i) $CH_3\text{-}OH$(Methanol) + HCOONa (Sodium formate)

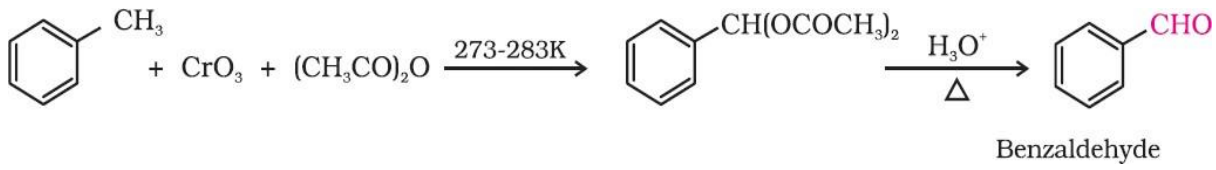
(ii) Refer the Answer of Question number 20 (iii)

*(iii) When toluene is oxidised using chromyl chloride (CrO_2Cl_2) in CS_2 followed by hydrolysis (acidification), we get benzaldehyde. This reaction is called **Etard reaction**.*



OR,

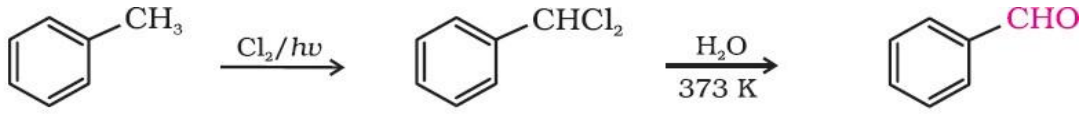
By treating toluene with chromic oxide in acetic anhydride, followed by acidification.



Benzaldehyde

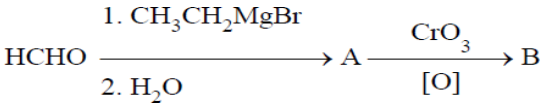
OR,

By Side chain chlorination of toluene followed by hydrolysis gives benzaldehyde.



Toluene Benzal chloride Benzaldehyde

47. (i) Predict A and B



(2)

(ii) Suggest a test to distinguish aldehydes and ketones. (1)

Ans: (i) A is CH_3-CH_2-CH_2-OH (Propan-1-ol or Propyl alcohol) and B is CH_3-CH_2-CHO (Propanal or Propionaldehyde)

(ii) Fehling's test or Tollen's test or Benedict's test.

48. (i) "Acyl chlorides can be reduced to give corresponding aldehydes."
Give the name of the reaction and catalyst used in the reaction. (2)
(ii) Distinguish between Aldol condensation and Cannizzaro reaction. (Any two differences) (2)
(iii) Among the following which is more acidic? Monochloroacetic acid or Monofluoroacetic acid? Justify your answer. (2) [SAY 2022]

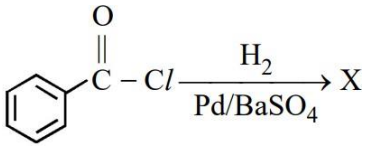
Ans: (i) Rosenmund's Reduction. Catalyst used is Pd supported on $BaSO_4$

(ii)

Aldol Condensation	***Cannizzaro reaction***
Given by aldehydes or ketones having atleast one α hydrogen atom.	*Given by aldehydes having no α hydrogen atom.*
Reagent used is dil. alkali	*Reagent used is conc. alkali*
The product formed is α,β-unsaturated aldehyde or ketone.	*The product formed is alcohol and salt of carboxylic acid.*

(iii) Monofluoro acetic acid. This is because of the greater electron withdrawing inductive effect of fluorine.

49. Identify the product 'X' in the chemical reaction given below: (1)



Ans: Benzaldehyde (C_6H_5-CHO) [Rosenmund's reduction]

50. (i) Write any two nucleophilic addition reactions of aldehyde. (2)
(ii) Name the product formed when ethanal is reduced with $LiAlH_4$. (1)

Ans: (i) Aldehydes undergo nucleophilic addition reaction with HCN and form cyanohydrins.

OR, R-CHO + HCN $\xrightarrow{OH^-}$ R-CHOH-CN

Aldehydes add alcohols to form hemi-acetals and acetals.

OR, R-CHO + R-OH $\xrightarrow{HCl}$ R-CH(OH)-OR $\xrightarrow{\quad\quad}$ R-CH(OR)$_2$

(ii) Ethanol or Ethyl alcohol [CH_3-CH_2-OH]

51. (i) Which one is more reactive among aldehydes and ketones ? (1)

(ii) Describe any two tests to distinguish aldehydes from ketones. (2)

Ans: (i) Aldehydes

(ii) (a) Tollen's test: When an aldehyde is heated with Tollens' reagent, we get a bright silver mirror.

(b) Fehling's test: When an aldehyde is heated with equal volume of Fehling's reagent A (aqueous solution of $CuSO_4$) and B (alkaline sodium potassium tartarate), we get a red precipitate of cuprous oxide (Cu_2O).

These tests are not answered by ketones.

52. (i) Explain Haloform reaction. (2)

(ii) How will you prepare benzaldehyde by Gattermann – Koch reaction ? (1)

(iii) Write the name of the reaction involved in the following conversion :

$$CH_3 - CO - CH_3 \xrightarrow{Zn-Hg\ \&\ Conc.HCl} CH_3 - CH_2 - CH_3 + H_2O$$ (1) *[March 2023]*

Ans: (i) Refer the answer of the question number 30.

(ii) Refer the answer of the question number 15 (b).

(iii) Clemmensen reduction

53. Name the product obtained when Toluene is treated with CrO_2Cl_2 in presence of CS_2.

(a) Benzaldehyde (b) Benzoic acid (c) Phenol (d) Chlorobenzene (1)

Ans: Benzaldehyde

54. (i) Give a test to distinguish aldehydes from Ketones. (1)

(ii) What is the reagent used in Clemmensen's reduction ? (1)

(iii) Describe Hell-Volhard-Zelinsky Reaction. (1)

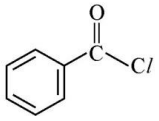
Ans: (i) Refer the answer of the question number 51 (ii)

(ii) zinc amalgam and conc. HCl

(iii) Refer the answer of the question number 20 (iii)

55. Identify the products X and Y in the following reactions. Also name these reactions.

(i)  $\xrightarrow[\text{Anhyd·}AlCl_3]{CO,\ HCl}$ X (1½)

(ii)  $\xrightarrow[Pd/BaSO_4]{H_2}$ Y (1½)

Ans: (i) Benzaldehyde [Gattermann Koch Reaction]

(ii) Benzaldehyde [Rosenmund's reduction]

56. (i) Name the product obtained when ethanal reacts with dilute NaOH. Write the chemical equation for the above reaction. (2)

(ii) What is the effect of substituents on the acidity of carboxylic acids ? (2) *[SAY 2023]*

Ans: (i) 3-Hydroxybutanal [CH_3-CH(OH)-CH_2-CHO]

$$2CH_3\text{-}CHO \xrightarrow{dil.\ NaOH} CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO$$

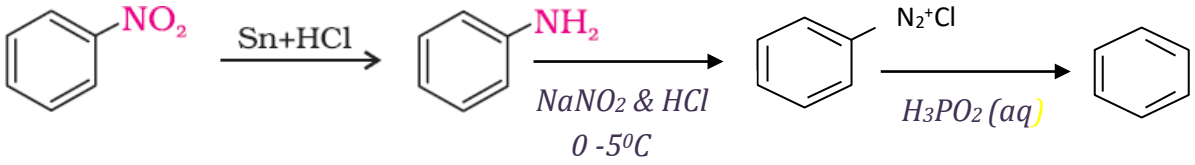
Ethanal *3-Hydroxybutanal*

(ii) Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the carboxylate ion. While electron donating groups decrease the acidity by destabilising the carboxylate ion.

Amines

1. A student was asked to convert nitrobenzene to benzene. Teacher suggested that he should first treat nitrobenzene with Sn and HCl and then proceed with the product obtained to get benzene. Write down the reaction involved in the above process. (3) [March 2009]

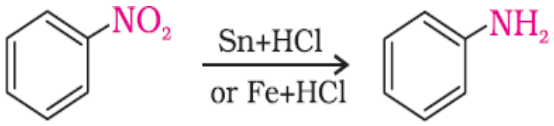
Ans:



2. Aromatic amines are important synthetic intermediates.
   a) What are the products obtained when aniline is treated with bromine water? (1)
   b) How will you convert nitrobenzene to aniline? (1)
   c) Write down the isocyanide test for the primary amines. (1) [March 2010]

Ans: a) 2,4,6-Tribromoaniline

b)



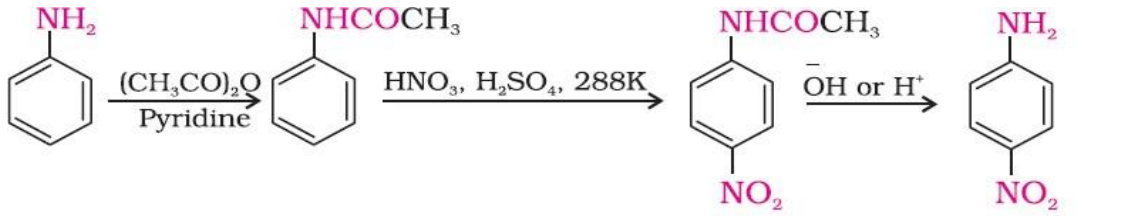
c) Primary amines on heating with chloroform and alcoholic potassium hydroxide form foul smelling isocyanides or carbylamines. This reaction is known as ***carbyl amine reaction or isocyanide test.***

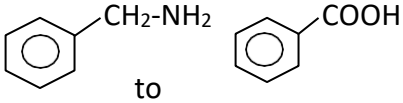
$$R\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{Heat} R\text{-}NC + 3\ KCl + 3\ H_2O$$

3. a) A student tried to prepare p-nitroaniline by nitrating Aniline with Conc. HNO_3 – Conc. H_2SO_4 mixture. But he got only m-nitroaniline. Why? (1½)
   b) Explain how he should proceed to get p-nitroaniline from aniline. (1½) [March 2011]

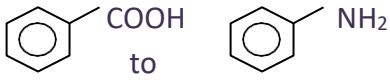
Ans: a) In strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. So a large amount of meta-nitroaniline is formed.

b) For the preparation of p-nitroaniline, the $-NH_2$ group is first deactivated by acetylation. The acetanilide thus formed is nitrated using nitrating mixture followed by hydrolysed.



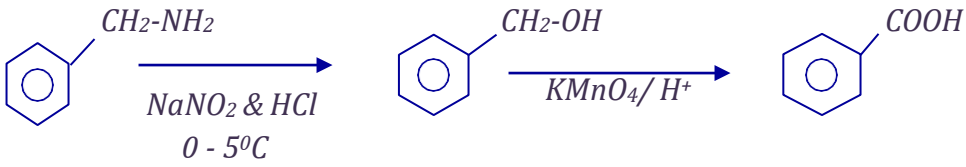
4. Amines are versatile functional group useful in the preparation of many organic compounds. How can you convert?
   i)  (1)

   to

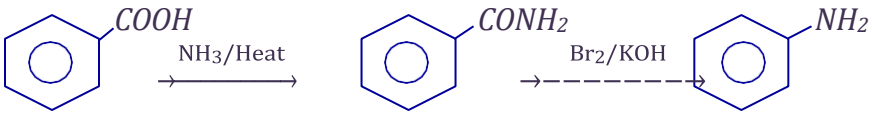
ii)  (2) [March 2011]

Ans:

(i) Benzyl amine on diazotisation gives a 1^0 alcohol, benzyl alcohol. This on oxidation using acidified $KMnO_4$, we get benzoic acid.

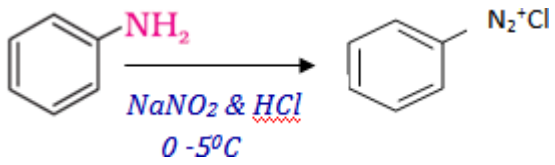


(ii) Benzoic acid on heating with ammonia we get benzamide which on treating with Bromine and alkali to form Benzoic acid.

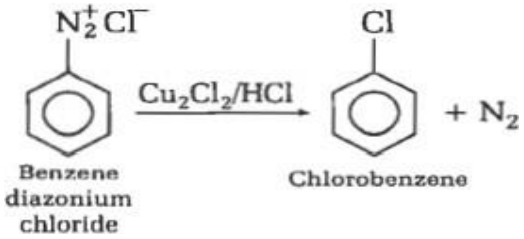


5. Aniline is an aromatic primary amine. Starting with aniline a number of organic compounds can be prepared.
   a) How is aniline converted to benzenediazonium chloride? (1)
   b) How are the following obtained from benzenediazonium chloride?
      i) Chlorobenzene ii) Phenol (2) [SAY 2011]

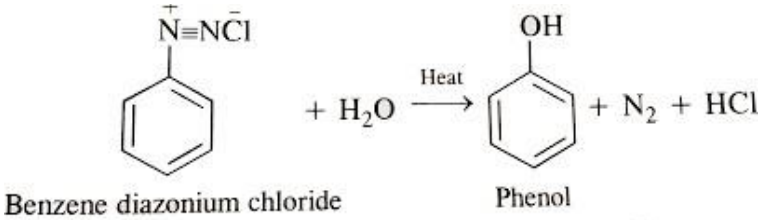
Ans: (a) Aniline on treating with $NaNO_2$ and HCl (or, with nitrous acid[HNO_2]) we get benzene diazonium chloride.



(b) (i) By treating benzenediazonium chloride with HCl in presence of cuprous chloride or Cu powder.



(ii) By warming benzenediazonium chloride with water.



6. Primary, secondary and tertiary amines can be distinguished by using Hinsberg's reagent.
   i) What is Hinsberg's reagent?
   ii) How will you distinguish primary, secondary and tertiary amines using this reagent? (3)
   [March 2012]

Ans: (i) Benzenesulphonyl chloride (C_6H_5-SO_2Cl)

(ii) Primary amines react with benzenesulphonyl chloride to form a precipitate of N-alkyl benzenesulphonamide, which is soluble in alkali.

Secondary amines react with benzene sulphonyl chloride to give a precipitate of N,N-dialkylbenzene sulphonamide, which is insoluble in alkali.

Tertiary amines do not react with benzenesulphonyl chloride

7. a) Carbyl amines have an offensive smell.
   i) Write the carbyl amine reaction. (1)
   ii) How will you convert aniline to phenol? (1)
   b) How will you convert an amide into following?
   i) An amine with one carbon atom less than that of the amide. (1)
   ii) An amine containing same number of carbon atom as that in the amide. (1) [SAY 2012]

Ans: a) Refer the Answer of the Question number 2.

b) (i) By Hoffmann bromamide degradation reaction [By treating with Br_2 and ethanolic NaOH]

(ii) By reduction using Lithium aluminium hydride ($LiAlH_4$).

8. Amines are basic in nature.
   a) Arrange the following compounds in the increasing order of their basic strength.
   NH_3, $C_6H_5NH_2$, $CH_3 - NH_2$, $(CH_3)_2NH$, $(CH_3)_3N$. (1)
   b) How will you convert aniline ($C_6H_5NH_2$) to chlorobenzene? (2) [March 2013]

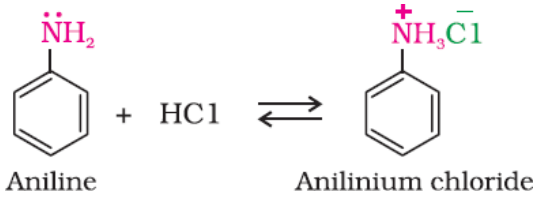
Ans: (a) $C_6H_5NH_2 < NH_3 < (CH_3)_3N < CH_3 - NH_2 < (CH_3)_2NH$

(b) Refer the Answer of the Question number 5.

9. Amines can be considered as derivatives of ammonia.
   a) Arrange the following amines in increasing order of their basic strength.
   $C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3. (1)
   b) Represent a reaction to explain the basic character of aniline. (1)
   c) Name the reagents used in the Hoffmann bromamide reaction. (½)
   d) What is the significance of the above reaction? (½)
   e) Give one chemical test to distinguish between methyl amine and dimethyl amine. Write down the chemical reaction. (1) [SAY 2013]

Ans: a) $C_6H_5NH_2 < NH_3 < C_2H_5 - NH_2 < (C_2H_5)_2NH$

b) Aniline reacts with HCl to form Anilinium chloride.



Aniline Anilinium chloride

c) Bromine and ethanolic NaOH or KOH.

d) The reaction is used to prepare amine containing one carbon less than that present in the amide.

e) Carbyl amine reaction. Methyl amine gives this reaction, while dimethyl amine does not.

$$CH_3\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{Heat} CH_3\text{-}NC + 3\ KCl + 3\ H_2O$$

10. a) Write a method of preparation of primary amines. (1)

b) Describe a chemical reaction given only by primary amines. (1)

c) What is diazotization? (1) [March 2014]

Ans: (a) Hoffmann bromamide degradation reaction.

(b) Carbyl amine reaction or Isocyanide reaction.

(c) Aniline on treating with $NaNO_2$ and HCl (or, with nitrous acid[HNO_2]) we get benzene diazonium chloride. This reaction is known as diazotisation.

11. a) Amines are basic. Arrange the following amines in the increasing order of base strength.

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$. (1)

b) Two well-known reactions are given below. Suggest the main product of each reaction.

i) $CH_3NH_2 \xrightarrow{CHCl_3 + alc.\ KOH}$

ii) $CH_3CONH_2 \xrightarrow{Br_2 + NaOH}$ (1 X 2 = 2) [SAY 2014]

Ans: a) $C_6H_5NH_2 < (CH_3)_3N < CH_3\text{-}NH_2 < (CH_3)_2NH$

b) (i) CH_3-NC (Methyl isocyanide). The reaction is Carbyl amine reaction or Isocyanide reaction.

(ii) $CH_3\text{-}NH_2$ (Methanamine). The reaction is Hoffmann bromamide degradation reaction.

12. Amines are classified as primary, secondary and tertiary.

a) Write the IUPAC name of the following compound: $H_2N\text{-}(CH_2)_6\text{-}NH_2$ (1)

b) Which is stronger base: $CH_3\text{-}NH_2$ or $C_6H_5\text{-}NH_2$? Why? (2) [March 2015]

Ans: a) Hexane-1,6-diamine

b) $CH_3\text{-}NH_2$. Due to the electron releasing inductive effect of CH_3 group, it will readily accept H^+ and hence it is more basic. [Or, In $C_6H_5\text{-}NH_2$, the lone pair of electrons is in conjugation with the benzene ring and it is less available for protonation. So it is less basic.]

13. a) Aromatic and aliphatic amines are basic in nature like ammonia. Arrange the following compounds in the increasing order of their basic strength: $CH_3\text{-}NH_2$, $(CH_3)_2NH$, NH_3, $C_6H_5\text{-}NH_2$ (1)

b) How will you carry out the following reactions?

i) Hoffmann bromamide reaction ii) Carbyl amine reaction (2) [SAY 2015]

Ans: a) $C_6H_5NH_2 < NH_3 < CH_3\text{-}NH_2 < (CH_3)_2NH$

b) i) Hoffmann Bromamide degradation Reaction: Amides on treating with Bromine and ethanolic solution of NaOH to give amines.

$$R\text{-}CO\text{-}NH_2 + Br_2 + 4\ NaOH \longrightarrow R\text{-}NH_2 + Na_2CO_3 + 2\ NaBr + 2\ H_2O$$

ii)** Carbyl amine Reaction: Primary amines on heating with chloroform and alcoholic potassium hydroxide form foul smelling isocyanides or carbylamines. This reaction is known as **carbylamine reaction or isocyanide test.

$$R\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{Heat} R\text{-}NC + 3\ KCl + 3\ H_2O$$

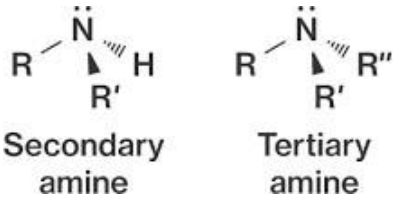
14. Amines are classified as primary, secondary and tertiary amine.

a) Represent the structure of secondary and tertiary amine. (1)

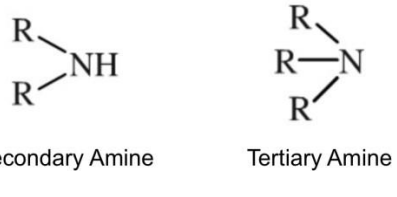
b) How will you convert nitrobenzene to aniline? (1)

c) Aniline does not undergo Friedel-Crafts reaction. Why? (1) [March 2016]

Ans: (a)



OR,



(b) Refer the Answer of the Question number 2 (a)

(c) Since the catalyst, $AlCl_3$, used in Friedel craft's reaction is a Lewis acid and Aniline is a Lewis base, they combine together to form salt. So the catalyst is not available for the reaction.

15. Amines are basic in nature.

a) Arrange the following compounds in the increasing order of their basic strength.

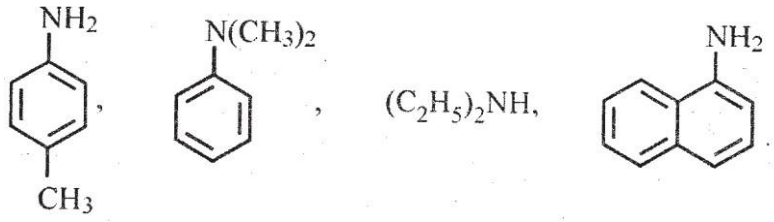
NH_3, $C_2H_5NH_2$, $C_6H_5NH_2$, $(C_2H_5)_2NH$ (1)

b) How will you convert aniline to chlorobenzene? (2) [SAY 2016]

Ans: a) Refer the Answer of the Question number 9 (a)

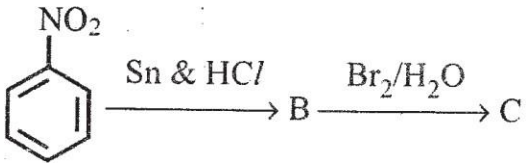
b) Refer the Answer of the Question number 5

16. a) Classify the following amines as primary, secondary and tertiary:



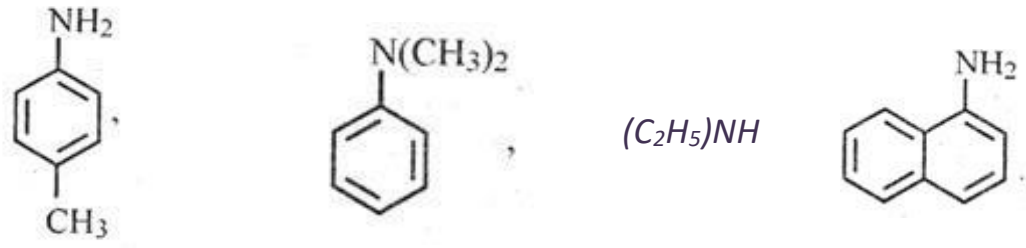
(1)

b)



Identify the products B and C write their formulae. (2) [March 2017]

Ans: a)



Primary amine *Secondary amine* *Secondary amine* *Primary amine*

b) B is Aniline (C_6H_5-NH_2) and B is 2,4,6 – Tribromoaniline

17. a) The most basic compound among the following is:

i) $C_2H_5NH_2$ ii) $C_6H_5NH_2$ iii) NH_3 iv) $(C_2H_5)_2NH$ (1)

b) Compound A is treated with Ethanolic NaCN to give the compound C_2H_5CN (B). Compound B on reduction gives compound C. Identify compounds A and C. (2) [SAY 2017]

Ans: a) $(C_2H_5)_2NH$

b) A is C_2H_5-Cl [Chloroethane] Or C_2H_5-Br[Bromoethane] and
C is C_2H_5-CH_2-NH_2 [Propan-1-amine]

18. Name the test used to identify primary amines using $CHCl_3$ and ethanolic KOH. (1)

Ans: Carbyl amine reaction or Isocyanide test

19. How can it convert methyl iodide to ethanamine? (2) [March 2018]

Ans: Methyl iodide + ethanolic KCN $\xrightarrow{\text{Reduction}}$ Ethane nitrile $\xrightarrow{\text{Reduction}}$ Ethanamine

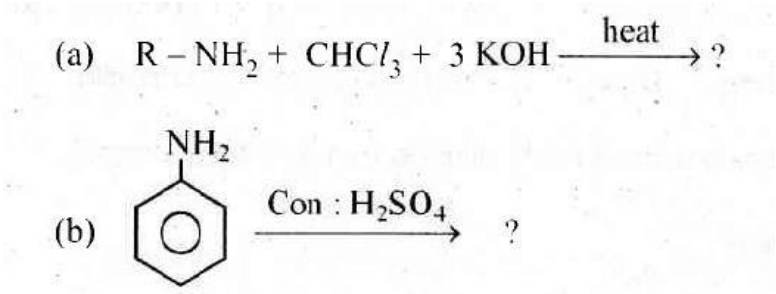
OR, $CH_3I + KCN(alc) \rightarrow CH_3$-CN $\xrightarrow{H_2/Ni}$ CH_3-CH_2-NH_2

20. Gabriel synthesis is used for the preparation of which type of amines?

i) Primary ii) Secondary iii) Tertiary iv) Quaternary (1)

Ans: (i) Primary

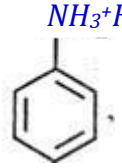
21. Complete the following equations:



(2) [SAY 2018]

Ans: (a) R-NC (Alkyl isocyanide or alkyl carbyl amine)

(b) Anilinium hydrogen sulphate [which n heating gives sulphanilic acid] OR,



22. The reaction in which an amide is converted into a primary amine by the action of Br_2 and alcoholic NaOH is known as …… (1)

Ans: Hoffmann Bromamide degradation Reaction

23. How is a primary amine distinguished from a secondary amine using a chemical test? (2) [March 2019]

Ans: Carbyl amine test: Primary amines on heating with chloroform and alcoholic potassium hydroxide form foul smelling isocyanides or carbylamines. This reaction is known as ***carbylamines reaction or isocyanide test.***

24. Explain the reaction of primary, secondary and tertiary amines with Hinsberg's reagent. (3) [SAY 2019]

Ans: Primary amines react with benzenesulphonyl chloride to form a precipitate of N-alkyl benzenesulphonamide, which is soluble in alkali.

Secondary amines react with benzene sulphonyl chloride to give a precipitate of N,N-dialkylbenzene sulphonamide, which is insoluble in alkali.

Tertiary amines do not react with benzenesulphonyl chloride

25. Complete the following table : (3x1=3)

Sl. No.	Reactant	Reagent	Product	Name of reaction
1.	$CH_3CH_2NH_2$	$CHCl_3$/KOH(aq)	……	Carbylamine reaction
2.	CH_3CONH_2	Br_2/KOH	CH_3NH_2	……
3.	……	$NaNO_2$+HCl/273K	$C_6H_5N_2^+Cl^-$	Diazotisation

[March 2020]

Ans:

Sl. No.	Reactant	Reagent	Product	Name of reaction
1.	$CH_3CH_2NH_2$	$CHCl_3$/KOH(aq)	*CH_3-CH_2-NC*	Carbylamine reaction
2.	CH_3CONH_2	Br_2/KOH	CH_3NH_2	*Hoffmann Bromamide degradation Reaction*
3.	*C_6H_5-NH_2*	$NaNO_2$+HCl/273K	$C_6H_5N_2^+Cl^-$	Diazotisation

26. (a) Amines are basic. Arrange the following amines in the increasing order of basic strength:

CH_3NH_2, $C_6H_5NH_2$, $(CH_3)_3N$, $(CH_3)_2NH$ (1)

(b) Benzene sulphonyl chloride and aqueous NaOH can be used to distinguish three classes of amines such as primary, secondary and tertiary.

(i) Name the above test. (1)

(ii) How will you distinguish between methyl amine and dimethyl amine using this test? (1) [SAY 2020]

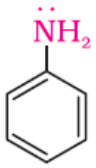
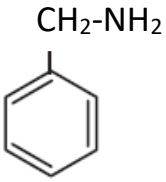
Ans: (a) Refer the Answer of the Question number 13 (a)

(b)(i) Hinsberg Test

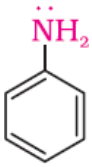
(ii) Methyl amine (which is a primary amine) react with benzenesulphonyl chloride to form a precipitate of N-methyl benzenesulphonamide, which is soluble in alkali.

Dimethyl amine(which is a secondary amine) react with benzene sulphonyl chloride to give a precipitate of N,N-dimethylbenzene sulphonamide, which is insoluble in alkali.

27. Which of the following amine cannot be prepared by Gabriel Phthalimide synthesis?

(A) CH_3-NH_2 (B)  (C) CH_3-CH_2-NH_2 (D) 

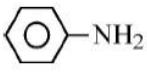
Ans: (B)



28. Explain the method to distinguish primary, secondary and tertiary amines. Also write the chemical equations involved. [March 2021]

Ans: Refer the Answer of the Question number 24

29. Identify A, B, C and D in the following reactions :

(i) $A \xrightarrow[NaOH]{Br_2}$  (1)

(ii) $CH_3 - CH_2 - NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} B + 3KCl + 3H_2O$ (1)

(iii)  $\xrightarrow{\text{Bromine Water}}$ C (1)

(iv)  $\xrightarrow{KI} D + KCl + N_2$ (1)

[SAY 2021]

Ans: (i) A is C_6H_5-CO-NH_2 (Benzamide)

(ii) B is CH_3-CH_2-NC (Ethyl isocyanide)

(iii) C is 2,4,6-Tribromoaniline

(iv) D is Iodobenzene or C_6H_5-I

30. A white precipitate is obtained when aniline reacts with bromine water at room temperature. The chemical name of the precipitate is_____. (1)

Ans: 2,4,6-Tribromoaniline

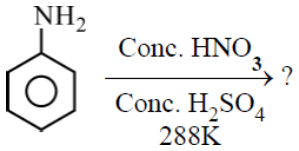
31. Explain carbylamine reaction with equation. (2)

Refer the Answer of the Question number 2 (c)

32. $CH_3 - NH_2$ is more basic than NH_3 while $C_6H_5 - NH_2$ is less basic than NH_3. Explain. (2) [March 2022]

Ans: Due to the electron releasing inductive effect of CH_3 group, it will readily accept H^+ and hence it is more basic. But in C_6H_5-NH_2, the lone pair of electrons is in conjugation with the benzene ring and it is less available for protonation. So it is less basic.]

33. Major product of the following reaction is:



(1)

Ans: p-Nitroaniline and m-Nitroaniline

34. (i) What is the chemical name of Hinsberg Reagent? (1)

(ii) Give the use of this reagent. (1)

Ans: (i) Benzene sulphonyl chloride is called Hinsberg reagent.

(ii) It is used to distinguish the 3 types of amines.

35. Arrange the following in the decreasing order of basic strength :

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2$ NH, NH_3. (2) [SAY 2022]

Ans: Refer the Answer of the Question number 9 (a).

36. Aniline does not undergo Friedel craft's reaction. Why ? (2)

Ans: Aniline (a Lewis base) forms salt with aluminium chloride (a Lewis acid), which is used as catalyst in Friedel Craft's reaction. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction. So it does not undergo Friedel-Crafts reaction.

37. (i) What is Carbylamine reaction ? (1)

(ii) Explain why aniline is less basic than ammonia. (2) [March 2023]

Ans: (i) Refer the Answer of the Question number 2 (c)

(ii) Aniline is less basic than ammonia due to the following reasons:

(i) In aniline (C_6H_5-NH_2), the lone pair of electrons is in conjugation with the benzene ring and hence it is less available for protonation.

(ii) Aniline is resonance stabilized. While, the anilinium ion formed by the protonation of aniline is not resonance stabilized. So aniline does not easily add proton, or it is less basic.

38. Identify X and Y in the following equations :

(i) $C_6H_5N_2Cl \xrightarrow{Cu/HCl} X + N_2 + CuCl$ **(1)**

(ii) $C_6H_5N_2Cl + H_2O \xrightarrow{\Delta} Y + N_2 + HCl$ **(1)**

Ans: (i) Chlorobenzene (C_6H_5-Cl)

(ii) Phenol (C_6H_5-OH)

39. (i) Aniline is less basic than ammonia. Why ? (2)

(ii) Name two reagents used to convert Nitrobenzene to aniline. (1) [SAY 2023]

Ans: (i) Refer the Answer of the Question number 37 (ii)

(ii) (a) Tin (Sn) & HCl [Or, iron & HCl] and

(b) H_2 gas in presence of Ni catalyst.

BIOMOLECULES

1. Glucose is commercially prepared from a polysaccharide.
   a) Which is the polysaccharide used for the production of glucose? (1)
   b) Name the process involved in the formation of glucose in the above method? (1) *[March 2008]*

   Ans: a) Starch
   b) Hydrolysis
2. Sucrose is fermented by yeast to ethyl alcohol. What are the enzymes used in this conversion? (2) *[SAY 2008]*

   Ans: Invertase and zymase
3. Carbohydrates are classified into three classes - monosaccharides, oligosaccharides and polysaccharides.
   a) What are polysaccharides? (1)
   b) Give two examples of polysaccharides? (1)
   c) What is invert sugar? (1)
   d) What is the basic structural difference between Starch and Cellulose? (1) *[March 2010]*

   Ans: a) Polysaccharides are carbohydrates which give a large number of monosaccharide units on hydrolysis.
   b) Starch and Cellulose
   c) The product obtained after the hydrolysis of cane sugar (sucrose) is called invert sugar. It is a mixture of D-(+)-glucose and D-(-)-fructose.
   d) Starch is a polymer of α-D-glucose, while Cellulose is a polymer of β-D-glucose.
4. a) Names of carbohydrates, their properties and structural patterns are given below. Match them properly. (2)

Glucose	Disaccharide	d-1,4 link
Sucrose	Reducing	Galactoxide
Lactose	Insoluble (in water)	1,6-linkage
Amylopectin	Non-reducing	Fructoxide
	Trisaccharide	Anomers present
	Monosaccharide	2-glucose units linked

   b) Proteins have polypeptide bonds. What are polypeptides? (1) *[March 2011]*

   Ans: a)

Glucose	*Monosaccharide Or, Reducing*	*Anomers present*
Sucrose	*Disaccharide Or, Non-reducing*	*Fructoxide*
Lactose	*Reducing Or, Disaccharide*	*Galactoxide*
Amylopectin	*Insoluble (in water)*	*1,6-linkage*

   b) If the number of amino acid molecules in a peptide is more than 10, it is called a polypeptide.
5. Proteins are the polymers of α-aminoacids. The structure and shape of proteins can be discussed at four levels, namely primary, secondary, tertiary and quaternary.
   Give an account of the structure and shape of proteins considering the above four levels. (3) *[SAY 2011]*

Ans: There are four types of structure for a protein. They are primary, secondary, tertiary and quaternary structure.

*1. **Primary structure**: It gives the sequence of amino acid molecules in a polypeptide chain of protein.*

*2. **Secondary structure**: It gives the different shapes in which polypeptide chain can exist. There are two different types of secondary structures - α-helix and β-pleated sheet structure.*

*3.**Tertiary structure**: It refers to the further folding of the secondary structure. It gives rise to two major molecular shapes - fibrous and globular.*

*4. **Quaternary structure**: Some of the proteins contain two or more polypeptide chains called sub-units. The spatial arrangement of these sub-units is known as quaternary structure.*

6. a) Carbohydrates are classified into monosaccharides, oligosaccharides and polysaccharides.

i) What is the basis of such classification? (1½)

ii) Give an example for an oligosaccharide. (½)

b) Vitamin 'C' is a vitamin found in fruits and vegetables. It cannot be stored in our body. Why? (1) *[March 12]*

Ans: a) (i) It is based on the behaviour on hydrolysis.

(ii) Sucrose or, maltose or, lactose.

b) Since vitamin C is water soluble, it cannot be stored in our body.

7. Proteins are important polymers of biological systems.

i) What is denaturation of proteins? (1)

ii) Give two examples of denaturation. (1) *[SAY 2012 & March 2009]*

Ans: i) When a protein is subjected to physical change (like change in temperature) or chemical change (like change in pH), it loses the biological activities. This process is called denaturation of protein.

ii) Coagulation egg white on boiling and curdling of milk.

8. a) Amino acids can be classified into essential amino acids and non essential amino acids.

i) What is the basis of such classification? (1)

ii) Write one example each for essential and non essential amino acids. (1)

b) Write any two differences between DNA and RNA. (1) *[March 2013]*

Ans: a) i) Based on the way by which an aminoacid is obtained in our body.

ii) E.g. for essential aminoacid is Lysine and for non-essential aminoacid is Glycine.

b)

DNA	*RNA*
The pentose sugar in DNA is 2-deoxy ribose	*The pentose sugar in RNA is ribose*
The nitrogen bases present in DNA are Adenine, Guanine, Cytosine and Thymine.	*In RNA, instead of Thymine, Uracil is present.*
DNA is double stranded	*RNA is single stranded*

[Any 2 differences required]

9. Name the products obtained in the following reactions.

a) $C_6H_{12}O_6$ $\xrightarrow{\text{Bromine water}}$ ..... (½)

b) $C_6H_{12}O_6$ $\xrightarrow{\text{HI/heat}}$ ..... (½)

c) What is invert sugar? (1)

d) Name two polysaccharides. (1) *[SAY 2013]*

Ans: a) Gluconic acid

b) n-Hexane

c) The product obtained after the hydrolysis of cane sugar (sucrose) is called invert sugar.

d) Starch and cellulose.

10. Biomolecules are formed by certain specific linkages between simple monomeric units. Write the names of linkages and monomeric units in the following class of biomolecules.

i) Starch ii) Protein iii) Nucleic acid (3) *[March 2014]*

Ans: i) Starch - Glycosidic linkage – α-D-glucose

ii) Protein - Peptide linkage – amino acid

iii) Nucleic acid – Phosphodiester linkage (H Bonds) - nucleotide

11. a) Name a fat soluble vitamin. Suggest a disease caused by its deficiency. (1)

b) What do you mean by the following:

i) Secondary structure of proteins.

ii) Nucleosides. (1 x 2 = 2) *[SAY 2014]*

Ans: a) Vitamin D. Deficiency disease is Rickets.

[Vitamin A, D, E & K are fat soluble]

b) i) Secondary structure gives the different shapes in which polypeptide chain can exist in a protein. There are two different types of secondary structures - α-helix and β-pleated sheet structure.

ii) In nucleic acids, the pentose sugar combines with the nitrogen base to form nucleosides.

12. Carbohydrates are broadly divided into monosaccharides, oligosaccharides and polysaccharides.

a) Write one example each of monosaccharide and oligosaccharide. (1)

b) i) Write any one method of preparation of glucose. (1)

ii) What is a peptide linkage? (1) *[March 2015]*

Ans: a) Glucose is a monosaccharide and sucrose is an oligosaccharide.

b) i) Fermentation of cane sugar

ii) –CO-NH- linkage in protein is called peptide bond.

13. a) Match the following structures of proteins in column I with their characteristic features in column II

Column I	**Column II**
i) Primary structure	a) Spatial arrangement of polypeptide sub units
ii) Secondary structure	b) Structure of amino acids
iii) Tertiary structure	c) Folding of peptide chains
iv) Quaternary structure	d) Sequence of amino acids
	e) Fibrous or globular nature

(2)

b) What is denaturation of proteins? (1) *[SAY 2015]*

Ans: a)

Column I	***Column II***
i) Primary structure	*d) Sequence of amino acids*
ii) Secondary structure	*c) Folding of peptide chains*
iii) Tertiary structure	*e) Fibrous or globular nature*
iv) Quaternary structure	*a) Spatial arrangement of polypeptide sub units*

b) Refer the Answer of the Question number 7 (i)

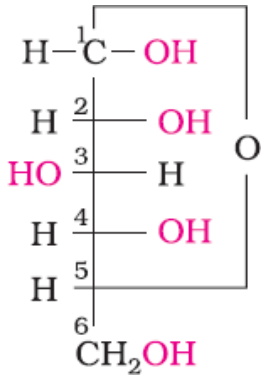
14. Cane Sugar, Glucose and Starch are Carbohydrates.

a) Represent the structure of Glucose. (1)

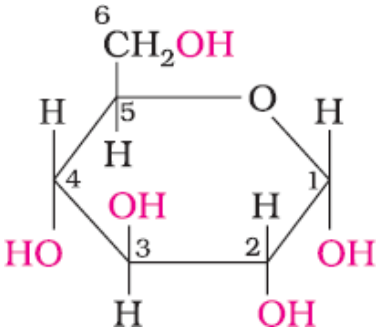
b) Write a method to prepare Glucose from Starch. Write the chemical equation of the reaction. (1)

c) Suggest any two uses of Carbohydrates. (1) *[March 2016]*

Ans: a)



α-D-(+)-Glucose



α-D-(+)-Glucopyranose

b) Glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6$$

c) Carbohydrates are used as raw materials for many important industries like textiles, paper, lacquers and breweries. Carbohydrate in the form of wood is used for making furniture etc.

15. Proteins are Biomolecules.

a) What is denaturation of protein? (1)

b) Match the following:

Vitamin A	Glucose
Starch	Zymase
Aldohexose	Night blindness
Enzyme	Amylose
	Fructose

(2) *[SAY 2016]*

Ans: a) Refer the Answer of the Question number 7 (ii)

b) Vitamin A — Night blindness
Starch — Amylose
Aldohexose — Glucose
Enzyme — Zymase

16. a) Which of the following is a polysaccharide?

i) Maltose ii) sucrose iii) fructose iv) cellulose (1)

b) Explain the amphoteric behaviour of aminoacid. (2) *[March 2017]*

Ans: a) Cellulose

b) Amino acids contain both acidic (carboxyl group) and basic (amino group) groups. In aqueous solution, they form internal salts known as zwitter ions. In zwitter ionic form, amino acids show amphoteric behaviour.

17. a) α-D-(+) glucose and β-D-(+) glucose are:

i) Metamers ii) Anomers iii) Geometrical isomers iv) Functional group isomers (1)

b) What is denaturation of proteins? (1)

c) Differentiate between nucleoside and nucleotide. (1) *[SAY 2017]*

Ans: a) Anomers

c) Refer the Answer of the Question number 7 (i)

d) Nucleoside is formed by the combination of pentose sugar with nitrogen base. Nucleoside combines with phosphoric acid unit to form nucleotide.

18. Which among the given vitamins is water soluble?

a) A b) B c) D d) E (1)

Ans: B

19. State two differences between globular and fibrous proteins. (2) *[March 2018]*

Ans:

Fibrous protein	***Globular protein***
It has fibre-like shape	*It has spherical shape*
It is water insoluble	*It is water soluble*
Here the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds.	*Here the chains of polypeptides coil around to give a spherical shape.*
E.g.: Keratin and myosin	*E.g. Insulin and albumins.*

[Any 2 differences required]

20. Which vitamin is responsible for blood clotting? (1)

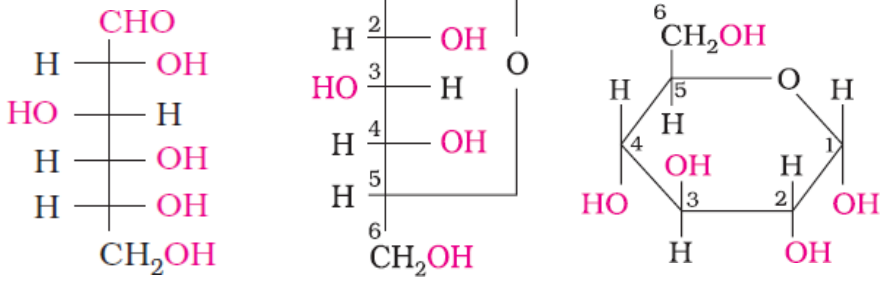
Ans: Vitamin K

21. Describe primary and secondary structure of proteins. (2) *[SAY 2018]*

Ans: Refer the Answer of the Question number 5.

22. Give the open chain and ring structures of glucose and account for the existence of glucose in two anomeric forms. (3) *[March 2019]*

Ans:



Open chain structure *Ring Structures*

The existence of glucose in two anomeric forms can be explained by the formation of 1,5-ring structure. Now the first carbon also becomes asymmetric and hence glucose exists in two anomeric forms. The structure in which -OH group of 1st carbon on the same side of the ring is called α–form and that on the opposite side of the ring is called β–form.

23. Write any three differences of RNA and DNA. (3) *[SAY 2019]*

Ans: Refer the Answer of the Question number 8 (b)

24. (a) Differentiate between globular and fibrous proteins. (2)

(b) The deficiency of which vitamin causes night-blindness. (1) *[March 2020]*

Ans: (a) Refer the Answer of the Question number 19.

(b) Vitamin A

25. Glucose is commercially prepared from polysaccharide.

(a) Which is the polysaccharide used for the production of glucose? (1)

(b) Give two examples for disaccharides. (1)

(c) What is invert sugar? (1) *[SAY 2020]*

Ans: (a) Starch

(b) Sucrose and Lactose

(c) The product obtained after the hydrolysis of cane sugar (sucrose) is called invert sugar. It is a mixture of D-(+)-glucose and D-(-)-fructose.

26. (i) Classify the following into monosaccharides and disaccharides:

Ribose, Fructose, Maltose, Sucrose. (1)

(ii) How is starch different from glycogen? (1)

(iii) Name the two hormones which work together to regulate glucose level in the body. (1) *[March 2021]*

Ans: (i) Monosaccharides: Ribose, Fructose

Disaccharides: Maltose, Sucrose.

(ii) Starch is the storage polysaccharide of plants while glycogen is the storage polysaccharide of animals.

(iii) Insulin and glucagon.

27. (i) Explain the classification of proteins based on their molecular shape. (2)

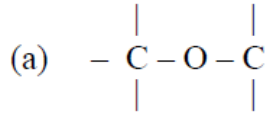
(ii) What is meant by denaturation of protein? (1) *[SAY 2021]*

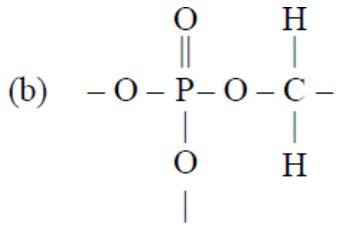
Ans: (i) Based on molecular structure, proteins are classified into two – fibrous and globular proteins. Fibrous proteins have fibre – like structure. Here the linear polypeptide chains are held together by H-bond and disulphide bond. They are generally insoluble in water. E.g. Keratin and myosin.

In Globular proteins the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. E.g.: Insulin and albumins.

(ii) Refer the Answer of the Question number 7 (i)

28. Identify the peptide bond among the following :

(a) 

(b) 

(c) – CO – NH –

(d) – COO –

(1)

Ans: -CO-NH-

29. (i) What are oligosaccharides? Give an example. (2)

(ii) What is glycogen? (1)

(iii) Explain the chemical constitution of starch. (1) *[March 2022]*

Ans: (i) Oligosaccharides are carbohydrates which give two to ten monosaccharide units on hydrolysis.

E.g. Sucrose, maltose, lactose.

(ii) Glycogen is the storage polysaccharide of animals. It is also known as animal starch.

(iii) Starch is a polymer of α-glucose and consists of two components - Amylose and Amylopectin.

30. The carbohydrate stored in liver, muscles and brain of animals is_____. (1)

Ans: Glycogen

31. (i) What is the glycosidic linkage in carbohydrates? (2)

(ii) How can you prepare glucose from sucrose? Why sucrose is a non-reducing sugar? (2) *[SAY 2022]*

Ans: (i) C-O-C linkage present in oligosaccharides and polysaccharides is called glycosidic linkage.

***Or,** in a disaccharide or polysaccharide, the monosaccharides are joined together through oxide linkage by losing water molecules. Such a linkage (C-O-C) between monosaccharide units through oxygen atom is called glycosidic linkage.*

(ii) Glucose is prepared by the hydrolysis of sucrose in presence of dil. mineral acids.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

In Sucrose, the reducing groups of glucose and fructose (aldehydic and ketonic groups) are involved in glycosidic bond formation. So it is non-reducing.

32. What are oligosaccharides ? Give any two examples. (2)

Ans: Refer the answer of the Question number 29 (i)

33. (i) What are essential and non-essential amino acids ? (1)

(ii) Explain the amphoteric behaviour of amino acids. (2) *[March 2023]*

Ans: (i) Aminoacids which are not synthesized in our body and should be obtained through diet are called essential aminoacids. E.g. Lysine

Aminoacids which are synthesized in our body are called non-essential aminoacids. E.g. Glycine

(ii) Refer the answer of the Question number 16 (b).

34. What do you mean by denaturation of proteins ? (2)

Refer the answer of the Question number 7 (i)

35. (i) What are polysaccharides ? Give two examples. (2)

(ii) Name the products of Hydrolysis of sucrose. (1) *[SAY 2023]*

Ans: (i) Refer the answer of the Question number 3 (a)

(ii) Glucose and fructose.