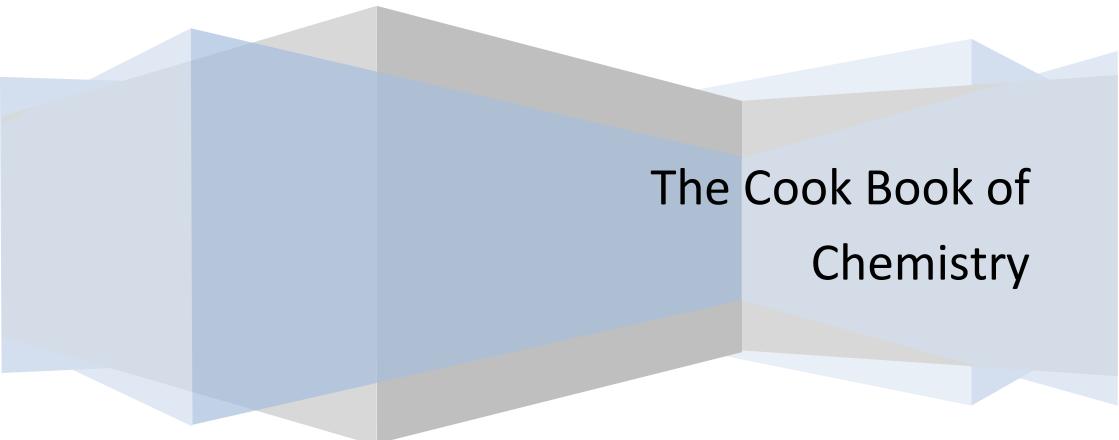


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The Cook Book of Chemistry

States of Matter

States of Matter

Single-Answer MCQ

(4) decrease in mean free path

[1992]

4. A gas behaves most like an ideal gas under conditions of :

(1) high pressure and low temperature

(2) high temperature and high pressure

(3) low pressure and high temperature

(4) low pressure and low temperature

[1993]

5. If C_1, C_2, C_3, \dots Represent the speeds of n_1, n_2, n_3, \dots Molecules, then the root mean square speed is:

$$(1) \left[\frac{n_1 C_1^2 + n_2 C_2^2 + n_3 C_3^2 + \dots}{n_1 + n_2 + n_3 + \dots} \right]^{1/2}$$

$$(2) \left[\frac{n_1^2 C_1^2 + n_2^2 C_2^2 + n_3^2 C_3^2 + \dots}{n_1 + n_2 + n_3 + \dots} \right]^{1/2}$$

$$(3) \frac{(n_1 C_1^2)^{1/2}}{n_1} + \frac{(n_2 C_2^2)^{1/2}}{n_2} + \frac{(n_3 C_3^2)^{1/2}}{n_3} + \dots$$

$$(4) \quad \left[\frac{(n_1 C_1 + n_2 C_2 + n_3 C_3 + \dots)^2}{(n_1 + n_2 + n_3 + \dots)} \right]^{1/2}$$

[1993]

[1996]

7. A gas will approach ideal behaviour at :

(1) low T and high P (2) low T and low P

(3) high T and low P (4) high T and high P

[1999]

[2000]

9. The rms speed of hydrogen is $\sqrt{7}$ times the rms speed of nitrogen. If T is the temperature of the gas, then :

(1) $T_{H_2} = T_{N_2}$ (2) $T_{H_2} > T_{N_2}$

(3) $T_{H_2} < T_{N_2}$ (4) $T_{H_2} = \sqrt{7} T_{N_2}$

[2000]

10. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as :

(1) d^2 (2) d

(3) \sqrt{d} (4) $\sqrt{1/d}$

[2001]

11. When the temperature is increased, surface tension of water :

(1) increases

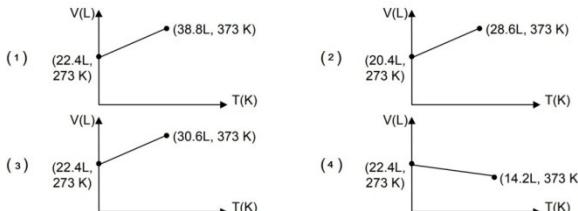
(2) decreases

(3) remains constant

(4) shows irregular behaviour

[2002]

12. Which of the following volume (V), temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmosphere ?



[2002]

13. Positive deviation from ideal behaviour takes place because of :

- (1) molecular interaction between atoms and $PV/nRT > 1$
- (2) molecular interaction between atoms and $PV/nRT < 1$
- (3) finite size of atoms and $PV/nRT > 1$
- (4) finite size of atoms and $PV/nRT < 1$

[2003]

14. For 1 mole of gas, the average kinetic energy is given as E . The u_{rms} of gas is :

(1) $\left[\frac{2E}{M} \right]^{1/2}$

(2) $\left[\frac{3E}{M} \right]^{1/2}$

$$(3) \left[\frac{2E}{3M} \right]^{1/2}$$

$$(4) \left[\frac{3E}{2M} \right]^{1/2}$$

[2004]

15. The ratio of rate of diffusion of helium and methane under identical conditions of pressure and temperature is :

(1) 4

(2) 2

(3) 1

(4) 0.5

[2005]

16. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equal to unity. The molar heat capacity of the gas is :

(1) $4R/2$

(2) $3R/2$

(3) $5R/2$

(4) zero

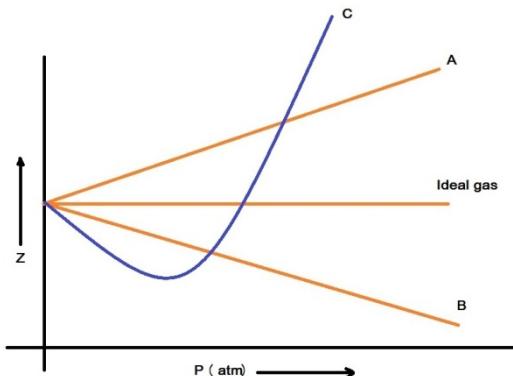
[2006]

Multiple Answer MCQ

1. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to :
- (1) increase in average molecular speed
 - (2) increased rate of collisions amongst molecules
 - (3) increase in molecular attraction
 - (4) decrease in mean free path

[1992]

2. The given graph represents the variation of Z (compressibility factor) v.s. P for three real gases A, B and C. Identify the correct statements.



- (1) For the gas A, $a = 0$ and its dependence on P is linear at all pressure.
 - (2) For the gas B, $b = 0$ and its dependence on P is linear at all pressure
 - (3) For the gas C, which is typical real gas for which $a \neq 0$, $b \neq 0$. By knowing the minima and the point of intersection with $Z = 1$, a and b can be calculated
 - (4) At high pressure, the slope is positive for all real gases. **[2008]**
3. A gas described by van der walls' equation : **[2008]**
- (1) behaves similar to an ideal gas in the limit of large molar volumes
 - (2) behaves similar to an ideal gas in the limit of large pressure
 - (3) is characterised by van der walls' coefficients that are dependent on the identity of gas but are independent of the temperature
 - (4) has the pressure that is lower than the pressure exerted by the same gas behaves ideally

Atomic Structure

Single-Answer MCQ

1. A 3p-orbital has :

- (1) two non-spherical nodes
- (2) two spherical nodes
- (3) one spherical and one non-spherical node
- (4) one spherical and two non-spherical nodes

[1995]

2. The number of nodal planes in a p_x-orbital is :

- (1) 1
- (2) 2
- (3) 3
- (4) zero

[2000]

3. The electronic configuration of an element is 1s², 2s²2p⁶, 3s²3p⁶3d⁵, 4s¹. This represents its :

- (1) excited state
- (2) ground state
- (3) cationic form
- (4) anionic form

[2000]

Solutions

Solution : A solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits.

$$\text{Mass percentage (w/w)} = \frac{\text{Mass of the Solute}}{\text{Total mass of Solution}} \times 100$$

$$\text{Volume percentage (v/v)} = \frac{\text{Volume of the Solute}}{\text{Total Volume of Solution}} \times 100$$

$$\text{Mass by Volume percentage (w/v)} = \frac{\text{Mass of the Solute in g}}{\text{Volume of Solution in mL}} \times 100$$

Parts per million (ppm) =

$$\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

$$\text{Mole fraction } x_A = \frac{n_A}{n_A + n_B}$$

$$\text{Molarity } M = \frac{\text{Number of Moles of Solute}}{\text{Volume of Solution in Litres}}$$

In case of ionic compounds it is called **Formality**

$$\text{Normality } N = \frac{\text{Number of Gram Equivalents of Solute}}{\text{Volume of Solution in Litres}}$$

$$\text{Molality } m = \frac{\text{Number of Moles of Solute}}{\text{Mass of solvent in kg}}$$

Mass % , ppm , mole fraction and molality are independent of temperature , whereas molarity is a function of temperature. This is because volume depends on temperature and the mass does not.

Q. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

Q. Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution. Q. Calculate molality of 2.5g of ethanoic acid (CH_3COOH) in 75 g of benzene.

Q. Find the molarity and molality of a 15% solution of H_2SO_4
(density of $\text{H}_2\text{SO}_4 = 1.020 \text{ g cm}^{-3}$)

Q. A sugar syrup of weight 214.2g contains 34.2g of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Calculate i)molal concentration II)mole fraction of sugar in the syrup.

Solubility of a Solid in a Liquid at any temperature is defined as the maximum amount of the solute in grams which can dissolve in 100 g of the solvent to form the saturated solution at that temperature.

Solubility of Solids in Liquids depends on

- i) **Nature of the solute and solvent** : Like dissolves like. Polar dissolves polar. Non polar dissolves non polar.
- ii) **Temperature** : a) for endothermic dissolution solubility increases with temperature
b) for exothermic dissolution solubility decreases with temperature
- iii) **Pressure** : No Effect.

The solubility of any gas in a Liquid is the volume of gas in cc's (converted to S.T.P) that can dissolve in 1 cc of the liquid to form the saturated solution at the temperature of the experiment and under a pressure of one atmosphere.

Solubility of Gases in Liquids depends on

- i) **Nature of the gas and solvent** : Gases like H_2S and NH_3 are more soluble in polar solvents like water while gases like oxygen, nitrogen and carbon dioxide are more soluble in non polar solvents like ethyl alcohol.
- II) **Temperature** : Solubility decreases with increase of temperature.
- III) **Pressure** : On increasing the pressure, the solubility increases.

Henry's Law : The partial pressure of a gas in vapour phase (p) is directly proportional to the mole fraction (x) of the gas in the solution.

$$p_A = k_H x_A$$

Applications of Henry's Law

- 1) In the production of carbonated beverages.
- 2) In the deep sea diving.
- 3) In the function of lungs.

Q. The Henry's law constant for oxygen dissolved in water is 4.34×10^4 atm at $25^\circ C$. If the partial pressure of oxygen in air is 0.2 atm under atmospheric conditions , calculate the concentration (in moles per litre) of dissolved oxygen in water in equilibrium with air at $25^\circ C$.

Q. If N_2 gas is bubbled through water at 293 K , how many millimoles of N_2 gas would dissolve in 1 litre of water.
Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry' s law constant for N_2 at 293 K is 76.48 kbar.

Q. H_2S , a toxic gas with rotten egg like smell , is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195m, calculate Henry's Law Constant.

Raoult's Law states that for a solution of volatile liquids, the partial vapor pressure of each component in the solution is directly proportional to its mole fraction.

$$P_1 = p_1^o x_1$$

According to Dalton's Law of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution .

$$\begin{aligned} p_{\text{total}} &= p_1^o x_1 + p_2^o x_2 = p_1^o + (p_2^o - p_1^o) x_2 \\ p_i &= y_i p_{\text{total}} \end{aligned}$$

Q. Vapour pressure of chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of CHCl_3 and 40 g of CH_2Cl_2 at 298 K and , (ii) mole fractions of each component in vapour phase.

Q. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

The properties

- (1) relative lowering of vapour pressure of the solvent
- (2) depression of freezing point of the solvent
- (3) elevation of boiling point of the solvent
- (4) osmotic pressure of the solution.

All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called colligative properties.

Relative lowering of vapour pressure

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

Q. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol^{-1}) . Vapour pressure of the solution ,then, is 0.845 bar. What is the molar mass of the solid substance?

Q. Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Elevation of boiling point

K_b is called **boiling point elevation constant or Molal Elevation Constant (Ebullioscopic Constant)**

$$\Delta T_b = K_b m$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H}$$

Q. 18 g of glucose , $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar?
 K_b for water is $0.52 \text{ K kg mol}^{-1}$

Q. 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 354.11 K . Calculate the molar mass of the solute. K_b for benzene is 2.53 K Kg mol⁻¹

Q. Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C. K_b for water is 0.52 K kg mol⁻¹

Depression of freezing point

K_f is called Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant.

$$\Delta T_f = K_f m$$

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H}$$

Q. 45 g of ethylene glycol C₂H₆O₂ is mixed with 600 g of water . Calculate (a) the freezing point depression and (b) the freezing point of the solution. K_f for water is 1.86 K kg mol⁻¹

Q. 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K . The freezing point depression constant of benzene is $5.12 \text{ K kg mol}^{-1}$. Find the molar mass of the solute.

Q. Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C . $K_f = 3.9 \text{ K kg mol}^{-1}$

Osmotic pressure

$$\Pi = (n_2/V) R T$$

Q. 200 cm³ of an aqueous solution of a protein contains 1.26g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar . Calculate the molar mass of the protein. ($R=0.083\text{Lbar mol}^{-1}\text{K}^{-1}$)

Q Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 ml of water at 37°C.

Abnormal molar mass

$$i = \frac{\text{Normal Molar Mass}}{\text{Abnormal Molar Mass}}$$

$$i = \frac{\text{Observed Colligative property}}{\text{Calculated Colligative property}}$$

$$i = \frac{\text{Total number of moles of particle after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

$$\frac{p_1^0 - p_1}{p_1^0} = i \frac{n_2}{n_1}$$

$$\Delta T_b = i K_b m$$

$$\Delta T_f = i K_f m$$

$$\Pi = i (n_2/V) R T$$

Q. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is $4.9 \text{ K kg mol}^{-1}$. What is the percentage association of acid if it forms dimer in solution?

Q. 0.6 mL of acetic acid (CH_3COOH), Having density 1.06 g mL^{-1} , is dissolved in 1 Litre of water. The depression in freezing point observed for this strength of acid was 0.205°C . Calculate the van't hoff factor and the dissociation constant of acid.

NCERT Exercise

2.1 Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

2.2 Suppose a solid solution is formed between two substances, one whose particles are very large and the other whose particles are very small. What kind of solid solution is this likely to be?

2.3 Define the following terms:

- (i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage.

2.4 Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1} ?

2.5 A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g mL^{-1} , then what shall be the molarity of the solution?

2.6 How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of both?

2.7 A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

2.8 An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} , then what shall be the molarity of the solution?

2.9 A sample of drinking water was found to be severely contaminated with chloroform (CHCl_3) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):

- (i) express this in percent by mass
- (ii) determine the molality of chloroform in the water sample.

2.10 What role does the molecular interaction play in a solution of alcohol and water?

2.11 Why do gases always tend to be less soluble in liquids as the temperature is raised?

2.12 State Henry's law and mention some important applications?

2.13 The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

2.14 What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{mix}}H$ related to positive and negative deviations from Raoult's law?

2.15 An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

2.16 Heptane and octane form an ideal solution. At 373 K , the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

2.17 The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

2.18 Calculate the mass of a non-volatile solute (molar mass 40 g mol⁻¹) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

2.19 A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate:
(i) molar mass of the solute (ii) vapour pressure of water at 298 K.

2.20 A 5% solution (by mass) of cane sugar in water has freezing point of 271K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.

2.21 Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate atomic masses of A and B.

2.22 At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?

2.23 Suggest the most important type of intermolecular attractive interaction in the following pairs.

- (i) n-hexane and n-octane
- (ii) I₂ and CCl₄
- (iii) NaClO₄ and water
- (iv) methanol and acetone
- (v) acetonitrile (CH₃CN) and acetone (C₃H₆O).

2.24 Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, CH₃OH, CH₃CN.

2.25 Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?

- (i) phenol (ii) toluene (iii) formic acid (iv) ethylene glycol (v) chloroform (vi) pentanol.

2.26 If the density of some lake water is 1.25g mL^{-1} and contains 92 g of Na^+ ions per kg of water, calculate the molality of Na^+ ions in the lake.

2.27 If the solubility product of CuS is 6×10^{-16} , calculate the maximum molarity of CuS in aqueous solution.

2.28 Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN .

2.29 Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5×10^{-3} M aqueous solution required for the above dose.

2.30 Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.

2.31 The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

2.32 Calculate the depression in the freezing point of water when 10 g of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86 \text{ K kg mol}^{-1}$.

2.33 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

2.34 Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.

2.35 Henry's law constant for the molality of methane in benzene at 298 K is $4.27 \times 10^5\text{ mm Hg}$. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg .

2.36 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr . Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr .

2.38 Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of naphthalene.

2.39 The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.

2.40 Determine the amount of CaCl_2 ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C .

2.41 Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25° C , assuming that it is completely dissociated.

Assignment

Problem 1. Calculate the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose per 150 mL solution.

[IITR 1985]

Problem 2. At 27°C, 36 g of glucose per litre has an O.P. of 4.92 atm. If the osmotic pressure of solution is 1.5 atm at the same temperature, what should be its concentration?

[IITR 1985]

Problem 3. (a) 10 g of a certain non-volatile solute were dissolved in 100 g water at 20°C. The vapour pressure was lowered from 17.3555 mm to 17.2350 mm, calculate m. wt. of solute.

(b) The vapour pressure of pure water at 25°C is 23.62 mm. What will be the vapour pressure of a solution of 1.5 g of urea in 50 g of water?

[IITR 2001]

Problem 4. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added 39.0 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molecular weight of solid substance.

[IIT 1990]

Problem 5. The vapour pressure of an aqueous solution of glucose is 750 mm of Hg at 373 K. Calculate molality and mole fraction of solute.

[IIT 1989]

Problem 6. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density 0.867 g mL^{-1}) increases by a factor of 7720 at 20°C . A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution

[IIT 1996]

Problem 7. A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg . Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene?

[IIT May 1997]

Problem 8. The vapour pressure of two miscible liquids (*A*) and (*B*) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (*A*) is mixed with 12 mole of (*B*). However, as soon as (*B*) is added, (*A*) starts polymerising into a completely insoluble solid. The polymerization follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg . Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution.

[IIT 2001]

Problem 9. 1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of a solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molecular weight of (A).

[IITR 2000]

Problem 10. The molal freezing point constant of C_6H_6 is 4.90 and its melting point is 5.51°C. A solution of 0.816 g of a compound A dissolved in 7.5 g of benzene freezes at 1.59°C. Calculate molecular weight of compound A.

[IITR 1989]

Problem 11. A solution of 0.643 g of an organic compound in 50 mL of benzene (density 0.879 g/mL) lowered its freezing point from 5.51 °C to 5.03°C. Calculate the molecular weight of solid. K_f for benzene is 5.12 K mol⁻¹ kg.

[IIT 1992]

Problem 12. A solution of a non-volatile solute in water freezes at - 0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K.

[IIT 1998]

Problem 13. To 500 cm^3 of water, $3.0 \times 10^{-3} \text{ kg}$ of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are $1.86 \text{ K kg mol}^{-1}$ and 0.997 g cm^{-3} respectively.

[IIT 2000]

Problem 14. The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute aqueous solution containing 7 g of salt

Per 100 g of water at 100°C is 70%. Calculate the vapour pressure of solution.

[IIT 1991]

Problem 15. 1.22 g of benzoic acid is dissolved in acetone and benzene separately. Boiling point of mixture with acetone increase by 0.17°C and boiling point of mixture with benzene increases by 0.13°C . .

K_b (acetone) = $1.7 \text{ K kg mol}^{-1}$, Mass of acetone = 100 g ;

K_b (benzene) = 2.6 K kg mol ; Mass of benzene = 100 g .

Find molecular weight of benzoic acid in acetone and in benzene solution. Justify your answer with structure.

[IIT 2004]

Problem 16. 75.2 g of $\text{C}_6\text{H}_5\text{OH}$ (phenol) is dissolved in 1 kg of solvent of $K_f = 14 \text{ K molality}^{-1}$. If depression in freezing point is 7K, Calculate % of phenol that dimerises.

[IIT 2006]

Objective

6. The elevation in boiling point of a solution of 13.44 g of CuCl_2 (molecular weight = 134.4, $K_b = 0.52 \text{ K molality}^{-1}$) in 1kg water using the following information will be

7. Which aqueous solution exhibits highest boiling point:

- (a) $0.015M$ glucose (b) $0.01M$ KNO_3 (c) $0.015M$ urea
(d) $0.01M$ Na_2SO_4

8. Which liquid pair shows a positive deviation from Raoult's law:

- | | |
|--|--------------|
| (a) Acetone –chloroform
methanol | (b) Benzene– |
| (c) Water-nitric acid
hydrochloric acid | (d) Water– |

9. Which statement is false:

- (a) Two sucrose solutions of same molality prepared in different solvents have same ΔT_f
 - (b) Osmotic pressure, $\pi = MRT$
 - (c) Osmotic pressure for 0.01M aqueous solution: $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{Sucrose}$
 - (d) The vapour pressure of a component over a solution is proportional to its mole fraction

10. If α is the degree of dissociation of Na_2SO_4 - the van't Hoff factor (i) used for calculating molecular mass is :

- (a) $1 + \alpha$ (b) $1 - \alpha$ (c) $1 + 2\alpha$
 (d) $1 - 2\alpha$

11. Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g benzene and 46 g toluene in torr is:

12. Equimolar solutions of two non-electrolytes in the same solvent have:

- (a) Same b.pt. but different f.pt.
 - (b) Same f.pt. but different b.pt.
 - (c) Same b.pt. and same f.pt.
 - (d) Different b.pt. and different f.pt.

13. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water for this aqueous solution at $100^{\circ}C$ is:

14. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is:

- (a) $2/3$ (b) $1/3 \times 273/298$ (c) $1/3$
 (d) $1/2$

15. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol⁻¹) in the same

solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3} , molar mass of the substance will be :

- (a) 90.0 g mol^{-1} (b) 115.0 g mol^{-1} (c) 105.0 g mol^{-1} (d) 210.0 g mol^{-1}

16. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be :

- (a) 350 (b) 300 (c) 700
(d) 360

17. During depression of freezing point in a solution, the following are in equilibrium:

- (a) liquid solvent, solid solvent (b) liquid solvent, solid solute
(c) liquid solute, solid solute (d) liquid solute, solid solvent

18. A $0.004M$ solution of Na_2SO_4 is isotonic with a $0.01M$ solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is:

- (a) 25% (b) 50% (c) 75% \
(d) 85%

19. When 20 g of naphthoic acid ($\text{C}_{11}\text{H}_8\text{O}_2$) is dissolved in 50g of benzene ($K_f = 1.72 \text{ K kg mol}^{-1}$), a freezing point depression of 2 K is observed. The van't Haff factor (i) is:

- (a) 0.5 (b) 1.0 (c) 2.0
(d) 3.0

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of Chemistry

Solutions Test (IIT)

Q. Vapour pressure of chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of CHCl_3 and 40 g of CH_2Cl_2 at 298 K and , (ii) mole fractions of each component in vapour phase.

20 Marks

Q. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol^{-1}) . Vapour pressure of the solution ,then, is 0.845 bar. What is the molar mass of the solid substance?

20 Marks

Q. 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 354.11 K . Calculate the molar mass of the solute. K_b for benzene is 2.53 K Kg mol⁻¹

20 Marks

Q Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 ml of water at 37°C.

20 Marks

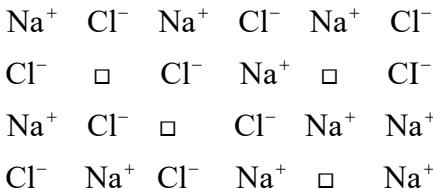
Q. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is $4.9 \text{ K kg mol}^{-1}$. What is the percentage association of acid if it forms dimer in solution?

20 Marks

The Solid State

Test- Solid State(Objective)

Note : Select the most suitable answer.



- (a) Frenkel and Schottky defects
(b) Schottky defect
(c) Interstitial defect
(d) Frenkel defect
4. An ionic compound has unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of cube. The empirical formula of this compound is :
- (a) AB (b) A₂B
(c) A₃B (d) AB₃
5. The volume of atoms present in a face centred cubic cell of a metal(r is atomic radius) is :
- (a) $\frac{20}{3}\pi r^3$ (b) $\frac{24}{3}\pi r^3$
(c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$
6. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face centred atoms along one of the axis are

removed, then the resultant stoichiometry of the solid is:

- (a) AB_2 (b) A_2B
(c) A_4B_3 (d) A_3B_4

7. A substance A_xB_y crystallizes in face centred cubic (fcc) lattice in which atoms A occupy each corner of the cube and atoms B occupy the centre of each face of the cube. The composition of A_xB_y is:

- (a) AB_3 (b) A_4B_3
(c) A_3B
(d) Can not be specified

8. In which of the following crystals alternate tetrahedral voids are occupied :

- (a) NaCl (b) ZnS
(c) CaF_2 (d) Na_2O

9. Match the column-I with column-II

Column-I

- (a) Simple cubic and face centred cubic

- (b) Cubic and rhombohedral
- (c) Cubic and tetragonal
- (d) Hexagonal and monoclinic

Column-II

- (p) have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma$
- (q) are two crystal system
- (r) have only two crystallography angles of 90°
- (s) belong to same crystal system

Solid State Test (CBSE)

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Marks for each question are indicated against each.
- (iii) Question nos. 1 to 8 are very short answer questions, carrying 1 mark each. Answer these in one word or about one sentence each.
- (iv) Question nos. 9 to 18 are short answer questions, carrying 2 marks each. Answer these in about 30 words each.
- (v) Question nos. 19 to 27 are short answer questions, carrying 3 marks each. Answer these in about 40 words each.
- (vi) Question nos. 28 to 30 are long answer questions, carrying 5 marks each. Answer these in about 70 words each.
- (vii) Use Log Tables, if necessary. Use of calculators is not permitted.

Q. 1. Name one solid which has both Schottky and Frenkel defects.

1 Marks

Q. 2. Arrange the following according to their packing fractions:

1 Marks

Simple cubic, face-centred cubic, body centred cubic

Q. 3. Why is Common salt sometimes yellow instead of being pure white?

1 Marks

Q. 4. Why is Frenkel defect not found in pure alkali metal halides?

1 Marks

Q. 5. A solid is hard, electrical insulator in the solid as well as molten state and melts at extremely high temperature. What type of solid is it ?

1 Marks

Q.6. A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

1 Marks

Q. 7. How does quartz glass differ from quartz?

1 Marks

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Q. 8. A metallic element crystallizes into a lattice containing a sequence of layers of ABABAB Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space?

1 Marks

Q.9. Why is glass considered as a supercooled liquid?

2 Marks

Q.10. Comment on the electrical conductivity of metals and semiconductors with increase of temperature.

2 Marks

Q.11. Distinguish between hexagonal and monoclinic unit cells.

2 Marks

Q.12. What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

2 Marks

Q.13. Non-stoichiometric cuprous oxide, Cu_2O can be prepared in the laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. Can you account for the fact that this substance is a p-type semiconductor?

2 Marks

Q.14. Gold (atomic radius = 0.144 nm) crystallizes in a face centered unit cell. What is the length of the side of the cell?

2 Marks

Q.15. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

2 Marks

Q.16. Classify each of the following as being either a p-type or n-type semiconductor giving reason.

2 Marks

(i) Ge doped with In

(ii) B doped with Si.

Q.17. In terms of band theory, what is the difference

2 Marks

(i) between a conductor and an insulator.

(ii) between a conductor and a semiconductor?

Q.18. Niobium crystallizes in a body centered cubic structure. If density is 8.55 g cm^{-3} , calculate atomic radius of niobium, given that its atomic mass is 93u.

2 Marks

Q.19. An element with molar mass $2.7 \times 10^{-2} \text{ kg mol}^{-1}$ forms a cubic unit cell with edge length 405 pm. If its density is $2.7 \times 10^3 \text{ kg m}^{-3}$, what is the nature of the cubic unit cell?

3 Marks

Q.20. If the radius of the octahedral void is r and the radius of the atoms in the close packing is R, derive relationship

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between rand R.

3 Marks

Q.21. Analysis shows that a metal oxide has the empirical formula of $M_{0.96}O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in this crystal.

3 Marks

Q.22. In an ionic compound, the anions (N) form cubic close type of packing while the cations (M) occupy one third of the tetrahedral voids. Deduce the empirical formula of the compound and the coordination number of (M) ions.

3 Marks

Q.23. The mineral haematite, Fe_2O_3 consists of a cubic close packed array of oxide ions with Fe^{3+} ions occupying interstitial positions. Predict whether the iron ions are in the octahedral or tetrahedral holes. Radius of $Fe^{3+} = 0.65\text{A}$ and that of $O^{2-} = 1.45\text{A}$.

3 Marks

Q.24. If NaCl is doped with 10^{-3} mol % $SrCl_2$ What is the concentration of cation vacancies?

3 Marks

Q.25. (a) 'Stability of a crystal is reflected in the magnitude of its melting point'. Comment.

(b) The melting points of some compounds are given below:

Water = 273 K, Ethyl alcohol = 155.7 K, Diethyl ether = 156.8 K, Methane = 90.5 K.

3 Marks

What can you say about the intermolecular forces between these molecules?

Q.26. Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous:

(i) Tetraphosphorus decoxide (P_4O_{10})

(ii) Ammonium phosphate, $(NH_4)_3PO_4$ (iii) SiC (iv) I_2 (v) P_4 (vi) Plastics (vii) Graphite (viii) Brass (ix) Rb

(x) LiBr (xi) Si

3 Marks

Q.27. How will you distinguish between the following pairs of terms?

3 Marks

(iii) Hexagonal close packing and cubic close packing

(iii) Crystal lattice and unit cell

(iii) Tetrahedral void and octahedral void.

Q.28. Account for the following:

5 Marks

(i) Silicon is an insulator but silicon doped with phosphorus acts as a semi-conductor.

(ii) Some of the glass objects recovered from ancient monuments look milky instead of being transparent.

(iii) FeO is non-stoichiometric with the formula $Fe_{0.95}O$,

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Q.29. Explain the difference between the following :

5 Marks

- (i) Ferromagnetism and antiferromagnetism
- (ii) n and p-type semiconductors.

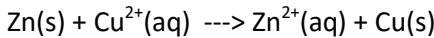
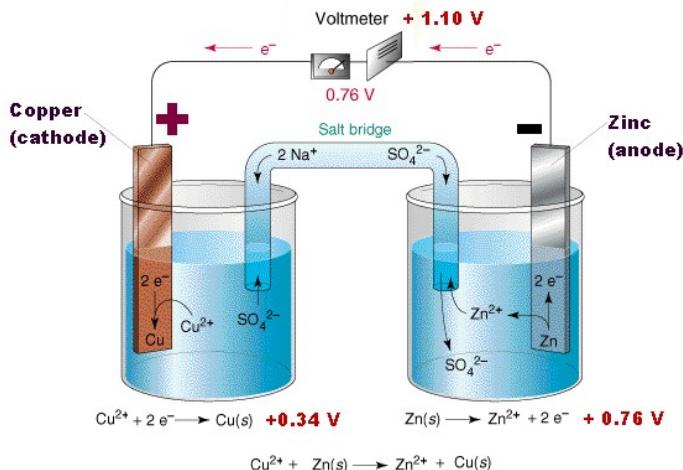
Q.30. Derive the expressions for the following:

5 Marks

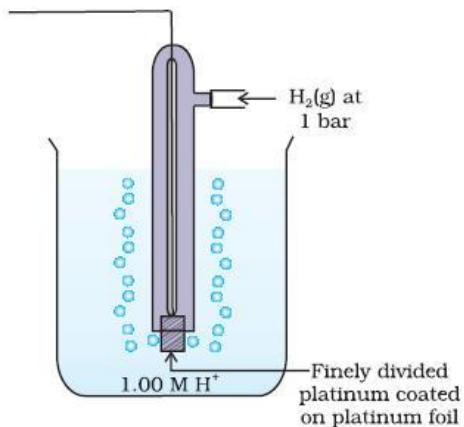
- (i) Density of a cubic crystal of an element of edge 'a' and atomic mass M.
- (ii) Packing efficiency of a body-centred cubic structure.

Electrochemistry

Galvanic Cells



$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$



Standard Hydrogen Electrode (SHE).

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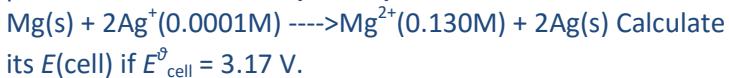
Reaction (Oxidised form + ne ⁻	→ Reduced form)	E ^o / V
F ₂ (g) + 2e ⁻	→ 2F ⁻	2.87
Co ³⁺ + e ⁻	→ Co ²⁺	1.81
H ₂ O ₂ + 2H ⁺ + 2e ⁻	→ 2H ₂ O	1.78
MnO ₄ ⁻ + 8H ⁺ + 5e ⁻	→ Mn ²⁺ + 4H ₂ O	1.51
Au ³⁺ + 3e ⁻	→ Au(s)	1.40
Cl ₂ (g) + 2e ⁻	→ 2Cl ⁻	1.36
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻	→ 2Cr ³⁺ + 7H ₂ O	1.33
O ₂ (g) + 4H ⁺ + 4e ⁻	→ 2H ₂ O	1.23
MnO ₂ (s) + 4H ⁺ + 2e ⁻	→ Mn ²⁺ + 2H ₂ O	1.23
Br ₂ + 2e ⁻	→ 2Br ⁻	1.09
NO ₃ ⁻ + 4H ⁺ + 3e ⁻	→ NO(g) + 2H ₂ O	0.97
2Hg ²⁺ + 2e ⁻	→ Hg ₂ ²⁺	0.92
Ag ⁺ + e ⁻	→ Ag(s)	0.80
Fe ³⁺ + e ⁻	→ Fe ²⁺	0.77
O ₂ (g) + 2H ⁺ + 2e ⁻	→ H ₂ O ₂	0.68
I ₂ + 2e ⁻	→ 2I ⁻	0.54
Cu ⁺ + e ⁻	→ Cu(s)	0.52
Cu ²⁺ + 2e ⁻	→ Cu(s)	0.34
AgCl(s) + e ⁻	→ Ag(s) + Cl ⁻	0.22
AgBr(s) + e ⁻	→ Ag(s) + Br ⁻	0.10
2H ⁺ + 2e ⁻	→ H ₂ (g)	0.00
Pb ²⁺ + 2e ⁻	→ Pb(s)	-0.13
Sn ²⁺ + 2e ⁻	→ Sn(s)	-0.14
Ni ²⁺ + 2e ⁻	→ Ni(s)	-0.25
Fe ²⁺ + 2e ⁻	→ Fe(s)	-0.44
Cr ³⁺ + 3e ⁻	→ Cr(s)	-0.74
Zn ²⁺ + 2e ⁻	→ Zn(s)	-0.76
2H ₂ O + 2e ⁻	→ H ₂ (g) + 2OH ⁻ (aq)	-0.83
Al ³⁺ + 3e ⁻	→ Al(s)	-1.66
Mg ²⁺ + 2e ⁻	→ Mg(s)	-2.36
Na ⁺ + e ⁻	→ Na(s)	-2.71
Ca ²⁺ + 2e ⁻	→ Ca(s)	-2.87
K ⁺ + e ⁻	→ K(s)	-2.93
Li ⁺ + e ⁻	→ Li(s)	-3.05

Nernst equation



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q. Represent the cell in which the following reaction takes place **(NCERT)**



Q. Calculate the emf of the cell in which the following reaction takes place **(NCERT)**



Given that $E^\theta_{\text{cell}} = 1.05 \text{ V}$

Equilibrium constant from Nernst Equation

$$E_{\text{cell}}^{\circ} = \frac{0.059V}{n} \log K_c$$

Q. Calculate the equilibrium constant of the reaction:

(NCERT)



$$E_{\text{cell}}^{\circ} = 0.46 \text{ V}$$

Gibbs Energy of Reaction

$$\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

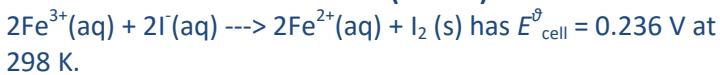
Q. The standard electrode potential for Daniell cell is 1.1V.
Calculate the standard Gibbs energy for the reaction:

(NCERT)



Q. The cell in which the following reaction occurs:

(NCERT)



Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Q. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

(NCERT)

Conductance of Electrolytic Solutions

$$R = \rho \frac{l}{A}$$

R = Resistance

ρ = Resistivity

$$G = \kappa \frac{A}{l}$$

G = Conductance

κ = Conductivity

$$G^* = \frac{l}{A} = \text{Cell Constant}$$

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

Q. Resistance of a conductivity cell filled with 0.1 mol L⁻¹ KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L⁻¹ KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L⁻¹ KCl solution. The conductivity of 0.1 mol L⁻¹ KCl solution is 1.29 S/m. (NCERT)

Q. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity and molar conductivity.

(NCERT)

Kohlrausch law of independent migration of ions

The law states that *limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.*

Ion	$\lambda^0 / (\text{S cm}^2 \text{mol}^{-1})$	Ion	$\lambda^0 / (\text{S cm}^2 \text{ mol}^{-1})$
H ⁺	349.6	OH ⁻	199.1
Na ⁺	50.1	Cl ⁻	76.3
K ⁺	73.5	Br ⁻	78.1
Ca ²⁺	119.0	CH ₃ COO ⁻	40.9
Mg ²⁺	106.0	SO ₄ ²⁻	160.0

Table
Limiting molar
conductivity for
some ions in
water at 298 K

Q. Calculate $\ddot{\Lambda}_m^0$ for CaCl₂ and MgSO₄ from the data given in Table **(NCERT)**

Q. \bar{E}_m° for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm² mol⁻¹ respectively. Calculate Λ° for HAc.

(NCERT)

$$\text{Degree of Dissociation } \alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

Q. The conductivity of $0.001028 \text{ mol L}^{-1}$ acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its dissociation constant if $\bar{\Lambda}_m^0$ for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$.

(NCERT)

Q. The molar conductivity of 0.025 mol L^{-1} methanoic acid is $46.1 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda_0(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda_0(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$

(NCERT)

Faraday's Laws of Electrolysis

First Law : The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

Second Law : The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal \div Number of electrons required to reduce the cation).

Q. A solution of CuSO_4 is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

(NCERT)

Q. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

(NCERT)

Q. Consider the reaction:

(NCERT)



What is the quantity of electricity in coulombs needed to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$?

NCERT Exercise

1. Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn.

2. Given the standard electrode potentials, $K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$, $Hg^{2+}/Hg = 0.79V$, $Mg^{2+}/Mg = -2.37 V$, $Cr^{3+}/Cr = - 0.74V$

Arrange these metals in their increasing order of reducing power.

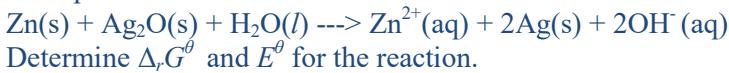
3. Depict the galvanic cell in which the reaction $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$ takes place. Further show:
- (i) Which of the electrode is negatively charged?
 - (ii) The carriers of the current in the cell.
 - (iii) Individual reaction at each electrode.

4. Calculate the standard cell potentials of galvanic cell in which the following reactions take place:
- (i) $2\text{Cr(s)} + 3\text{Cd}^{2+}(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Cd}$
 - (ii) $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag(s)}$
- Calculate the $\Delta_r G^\theta$ and equilibrium constant of the reactions.

5. Write the Nernst equation and emf of the following cells at 298 K:

- (i) Mg(s) | Mg²⁺(0.001M) || Cu²⁺(0.0001 M) | Cu(s)
- (ii) Fe(s) | Fe²⁺(0.001M) || H⁺(1M) | H₂(g)(1bar) | Pt(s)
- (iii) Sn(s) | Sn²⁺(0.050 M) || H⁺(0.020 M) | H₂(g) (1 bar) | Pt(s)
- (iv) Pt(s) | Br₂(l) | Br⁻(0.010 M) || H⁺(0.030 M) | H₂(g) (1 bar) | Pt(s).

6. In the button cells widely used in watches and other devices the following reaction takes place:



7. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity.

9. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$.

10. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

Concentration/M	0.001	0.010	0.020
0.050	0.100		
$10^2 \times \kappa/\text{S m}^{-1}$	1.237	11.85	23.15
55.53	106.74		

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of $\Lambda^{\circ}m$

11. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm⁻¹. Calculate its molar conductivity and if $\Lambda^{\circ}m$ for acetic acid is 390.5 S cm² mol⁻¹, what is its dissociation constant?

12. How much charge is required for the following reductions:

- (i) 1 mol of Al³⁺ to Al.
- (ii) 1 mol of Cu²⁺ to Cu.
- (iii) 1 mol of MnO₄⁻ to Mn²⁺.

13. How much electricity in terms of Faraday is required to produce

- (i) 20.0 g of Ca from molten CaCl_2 .
- (ii) 40.0 g of Al from molten Al_2O_3 .

14. How much electricity is required in coulomb for the oxidation of

- (i) 1 mol of H_2O to O_2 .
- (ii) 1 mol of FeO to Fe_2O_3 .

15. A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

16. Three electrolytic cells A,B,C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

17. Using the standard electrode potentials given in **Table** predict if the reaction between the following is feasible:

- (i) Fe^{3+} (aq) and I^- (aq)
- (ii) Ag^+ (aq) and Cu(s)
- (iii) Fe^{3+} (aq) and Br^- (aq)
- (iv) Ag(s) and Fe^{3+} (aq)
- (v) Br_2 (aq) and Fe^{2+} (aq).

18. Predict the products of electrolysis in each of the following:

- (i) An aqueous solution of AgNO_3 with silver electrodes.
- (ii) An aqueous solution of AgNO_3 with platinum electrodes.
- (iii) A dilute solution of H_2SO_4 with platinum electrodes.
- (iv) An aqueous solution of CuCl_2 with platinum electrodes.

Assignment

1. Copper sulphate solution (250 ml.) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minute. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

[IIT 2000]

2. Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation.



Calculate:

I. How many gram of chromium will be plated out by 24000 coulomb?

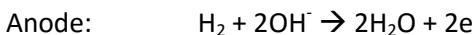
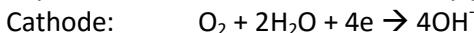
II. How long will it take to plate out 1.5 g of Cr by using 12.5 ampere current?

[IIT 1993]

3. Electrolysis of a solution of MnSO₄ in aqueous sulphuric acid is a method for the preparation of MnO₂ as per reaction,
 $Mn^{2+} \text{ (aq)} + 2H_2O \rightarrow MnO_2(s) + 2H^+ \text{ (aq)} + H_2(g)$
Passing a current of 27 ampere for 24 hour gives one kg of MnO₂. What is the value of current efficiency? Write the reaction taking place at the cathode and at the anode.

[IIT 1997]

4. In a fuel cell H₂ and O₂ react to produce electricity. In the process H₂ gas is oxidized at the anode and O₂ at cathode. If 67.2 litre of H₂ at STP reacts in 15 minute, what is average current produced? If the entire current is used for electro deposition of Cu from Cu²⁺, how many g of Cu are deposited?



[IIT 1988]

5. An aqueous solution of NaCl on electrolysis gives H₂(g), Cl₂(g) and NaOH according to reaction:



A direct current of 25 ampere with a current efficiency of 62 % is passed through 20 litre of NaCl solution (20% by weight).

- Write down the reactions taking place at the electrodes.
- How long will it take to produce 1 kg of Cl₂?
- What will be the molarity of solution with respect to OH⁻ ?

Assume no loss of volume due to evaporation.

[IIT 1992]

6. A current of 1.7 ampere is passed through 300 ml. of 0.160 M solution of ZnSO_4 for 230 sec with a current efficiency of 90%. Find the molarity of Zn^{2+} after the deposition of Zn. Assume the volume of the solution remains constant during electrolysis.

[IIT 1991]

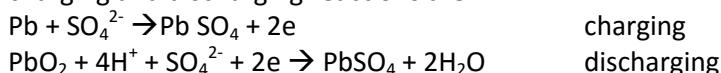
7. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml. and the current at 1.2 ampere. Calculate volume of gases evolved at NTP during entire electrolysis. At. Wt. of Cu=63.6

[IIT 1989]

8. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if current efficiency is 50%. If the potential drop across the cell is 3.0 volt, how much energy will be consumed?

[IIT 1990]

9. during the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 g ml^{-1} to 1.139 g ml^{-1} . sulphuric acid of density 1.294 g ml^{-1} is 39% by weight and that of density 1.139 g ml^{-1} is 20% by weight. The battery holds 3.5 litre of acid and the volume practically remained constant during the discharge. Calculate the no. of ampere hour for which the battery must have been used. The charging and discharging reactions are:

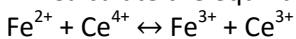


[IIT 1986]

10. How many grams of silver could be plated out on a serving tray by electrolysis of solution containing silver in +1 oxidation state for a period of 8.0 hour at a current of 8.46 ampere? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm³.

[IIT 1997]

11. Calculate the equilibrium constant for the reaction:



Given: $E^{\circ}_{\text{Ce4+}/\text{Ce3+}} = 1.44 \text{ V}$ and $E^{\circ}_{\text{Fe3+}/\text{Fe2+}} = 0.68 \text{ V}$

[IIT 1997]

12. The following electrochemical cell has been set up.



$$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{V} \text{ and } E^{\circ}_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.61\text{V}$$

If an ammeter is connected between the two platinum electrode, predict the direction of flow of current. Will the current increase or decrease with time?

[IIT 2000]

13. Calculate the equilibrium constant for the reaction, $2\text{Fe}^{3+} + 3\text{I}^- \leftrightarrow 2\text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for $\text{Fe}^{3+}|\text{Fe}^{2+}$ and $\text{I}_3^-|\text{I}^-$ couples.
[IIT 1998]

14. Zinc granules are added in excess to 500 ml of 1M $\text{Ni}(\text{NO}_3)_2$ solution at 25°C until the equilibrium is reached. If $E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ and $E^\circ_{\text{Ni}^{2+}/\text{Ni}}$ are -0.75V and -0.24V respectively, find out the $[\text{Ni}^{2+}]$ at equilibrium.

[IIT 1991]

15. The standard reduction potential for $\text{Cu}^{2+} \mid \text{Cu}$ is + 0.34V. Calculate the reduction potential at pH = 14 for the above couple, K_{SP} of $\text{Cu}(\text{OH})_2$ is 1.0×10^{-19} .

[IIT 1996]

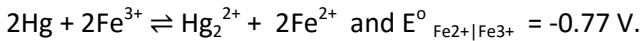
16. The standard reduction potential of $\text{Cu}^{2+}|\text{Cu}$ and $\text{Ag}^+|\text{Ag}$ electrodes are 0.337 V and 0.799 V respectively. Construct a galvanic cell using these electrodes so that its E_{cell}° is +ve. For what $[\text{Ag}^+]$ will the emf of cell at 25°C be zero if $[\text{Cu}^{2+}]$ is 0.01 M? [IIT 1990]

17. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the e.m.f. of the cell $\text{Ag} \mid \text{Ag}^+$ (satd. Ag_2CrO_4 sol.) || $\text{Ag}^+(0.1\text{M}) \mid \text{Ag}$ is 0.164 V at 298 K .

[IIT 1998]

18. The standard reduction potential at 25°C for the reaction $2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^-$ is -0.8277 V. Calculate the equilibrium constant for the reaction $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ at 25°C. [IIT 1989]

19. An excess of liquid Hg was added to 10^{-3} acidified solution of Fe^{3+} ions. It was found that only 5% of the ions remained as Fe^{3+} at equilibrium at 25°C . Calculate E° for $2\text{Hg} | \text{Hg}_2^{2+}$ at 25°C for



[IIT 1995]

20. A cell $\text{Ag} \mid \text{Ag}^+ \parallel \text{Cu}^{2+} \mid \text{Cu}$ initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 ampere of current for 1 hour.

[IIT 1999]

Objective

1. If Φ denotes standard reduction potential, which is true:
[AIEEE 2002]

- (a) $E_{\text{cell}}^{\circ} = \Phi_R - \Phi_L$
- (b) $E_{\text{cell}}^{\circ} = \Phi_L + \Phi_R$
- (c) $E_{\text{cell}}^{\circ} = \Phi_L - \Phi_R$
- (d) $E_{\text{cell}}^{\circ} = -(\Phi_L + \Phi_R)$

2. Emf of a cell in terms of reduction potential of its left and right electrodes is:
[AIEEE 2002]

- (a) $E = E_{\text{Left}} - E_{\text{right}}$
- (b) $E = E_{\text{Left}} + E_{\text{right}}$
- (c) $E = E_{\text{right}} - E_{\text{Left}}$
- (d) $E = -[E_{\text{right}} + E_{\text{Left}}]$

3. Conductance (Siemens, S) is directly proportional to the area of the vessel and the concentration of solution in it and is inversely proportional to the length of the vessel then, the unit of constant of proportionality is:
[AIEEE 2002]

- (a) $S \text{ m mol}^{-1}$
- (b) $S \text{ m}^2 \text{ mol}^{-1}$
- (c) $S^{-2} \text{ m}^1 \text{ mol}$
- (d) $S^2 \text{ m}^2 \text{ mol}^{-2}$

4. The emf of given cell Pt-H₂ | H⁺ | H₂-Pt is:



[AIEEE 2002]

- a) $(RF/F) \log (P_1/P_2)$
- b) $(RF/F) \log e (P_1/P_2)$
- c) $(RF/F) \log e (P_2/P_1)$
- d) None of these

5. The $E_{M/M}^{0, 3+ / 2+}$ values for Cr, Mn, Fe and Co are -0.41, +1.57, +0.77 and +1.97V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest:

[AIEEE 2003]

6. Standard reduction electrode potentials of three metals A, B and C are +0.5 V, -3.0 V and -1.2 V respectively. The reducing power of these metals are:

[AIEEE 2003]

- (a) $B > C > A$ (b) $A > B > C$
 (c) $C > B > A$ (d) $A > C > B$

7. For a cell reaction involving a two electron change, the standard e.m.f., of the cell is found to be 0.295V at 25°C. The equilibrium constant of the reaction at 25°C will be:

[AIEEE 2003]

- (a) 1×10^{-10} (b) 29.5×10^{-2}
 (c) 10 (d) 1×10^{10}

8. When during electrolysis of a solution of AgNO_3 , 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be:

[AIEEE 2003]

9. For the redox change;

[AIEEE 2003]

$\text{Zn}_{(s)} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}_{(s)}$, taking place in a cell E_{cell}° is 1.10 volt. E_{cell} for the cell would be:

0.1M 1M

10. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to : [AIEEE 2004]

- (a) remove adsorbed oxygen from electrode surfaces
 - (b) create potential difference between the two electrodes
 - (c) produce high purity water
 - (d) generate heat

11. Consider the following E° values. $E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77V$, $E^\circ_{Sn^{2+}/Sn} = -0.14 V$, The E°_{cell} for the reaction:



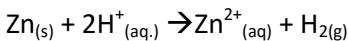
[AIEEE 2004]

12. The standard emf of a cell having one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is:

[AIEEE 2004]

- (a) 1.0×10^{30} (b) 1.0×10^5
 (c) 1.0×10^{10} (d) 1.0×10^1

13. In a cell that utilises the reaction;



addition of H_2SO_4 to cathode compartment will :

[AIEEE 2004]

- (a) increase the E and shift equilibrium to the left
 - (b) lower the E and shift equilibrium to the right

- (c) increase the E and shift equilibrium to the right
 - (d) lower the E and shift equilibrium to the left

14. The limiting molar conductivities Λ° for NaCl, KBr and KCl are 126, 152 and 150 $S\text{ cm}^2\text{ mol}^{-1}$ respectively. The Λ° for NaBr $S\text{ cm}^2\text{ mol}^{-1}$ is:

[AIEEE 2004]

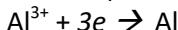
15. The highest electrical conductivity of the following aqueous solutions is of: [AIEEE 2005]

[AIEEE 2005]

16. The molar conductance of acetic acid at infinite dilution if Λ° for CH_3COONa , NaCl and HCl are 91.0, 126.5 and 426.2 $\text{S cm}^2 \text{ mol}^{-1}$ respectively:

[AIEEE 2005]

17. Aluminium oxide may be electrolysed at 1000°C to furnish Al metal (at. mass = 27 amu). The cathode reaction is:



How much electricity is required to prepare 5.12 kg of Al by this method? [AIEEE 2005]

- (a) 5.49×10^7 coulomb (b) 1.83×10^7 coulomb
 (c) 5.49×10^4 coulomb (d) 5.49×10^{10} coulomb

18. The molar conductivity $\Lambda^\circ_{\text{NaOAc}}$ and $\Lambda^\circ_{\text{HCl}}$ at infinite dilution in water at 25°C are 91.0, 426.2 S cm² mol⁻¹ respectively. To

calculate $\Lambda^\circ_{\text{HAc}}$, the additional value required is:

[AIEEE 2006]

- (a) $\Lambda^\circ_{\text{H}_2\text{O}}$ (b) $\Lambda^\circ_{\text{KCl}}$
 (c) $\Lambda^\circ_{\text{NaOH}}$ (d) $\Lambda^\circ_{\text{NaCl}}$

19. The ionic mobility of alkali metal ion in aqueous solution is maximum for: [AIEEE 2006]

20. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration $0.1M$ is 100 ohm . The conductivity of this solution is 1.29 S m^{-1} . Resistance of the same cell filled with $0.02M$ of the same solution if the electrolyte is 520 ohm . The molar conductivity of $0.02M$ solution of electrolyte would be :

[AIEEE 2006]

- (a) $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (b) $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (c) $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (d) $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

21. At 25°C, $\text{Ag} + \text{l}^- \rightarrow \text{Agl} + e;$ $E^\circ = 0.152\text{V}$

$$\text{Ag} \rightarrow \text{Ag}^+ + e; \quad E^\circ = -0.80\text{V}$$

The $\log K_{SP}$ of AgI is: $(2.303RT/F = 0.059V)$

[AIEEE 2006]

The Cook Book
of Chemistry

The Organic Chemistry

Haloalkanes

The replacement of hydrogen atom(s) in an aliphatic hydrocarbon, by halogen atom(s) results in the formation of alkyl halide (haloalkane). Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group.

Classification

1.) On the Basis of Number of Halogen Atoms

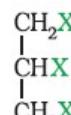
These may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,



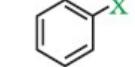
Monohaloalkane



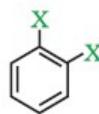
Dihaloalkane



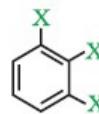
Trihaloalkane



Monohaloarene



Dihaloarene



Trihaloarene

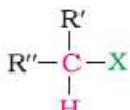
2.) Compounds Containing sp^3 C—X Bond (X= F, Cl, Br, I)

(a) Alkyl halides or haloalkanes (R—X)

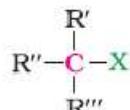
In alkyl halides, the halogen atom is bonded to an alkyl group (R). They form a homologous series represented by $\text{C}_n\text{H}_{2n+1}\text{X}$. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



Primary (1°)



Secondary (2°)



Tertiary (3°)

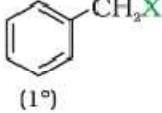
(b) Allylic halides

These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to carbon-carbon double bond ($\text{C}=\text{C}$) i.e. to an allylic carbon.

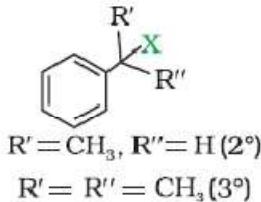


(c) Benzylic halides

These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to an aromatic ring.



(1°)



$\text{R}'=\text{CH}_3, \text{R}''=\text{H} (2^\circ)$

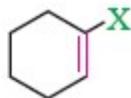
$\text{R}'=\text{R}''=\text{CH}_3 (3^\circ)$

3.) Compounds Containing sp^2 C—X Bond

This class includes:

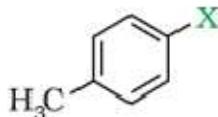
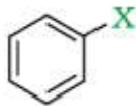
(a) Vinylic halides

These are the compounds in which the halogen atom is bonded to an sp^2 -hybridised carbon atom of a carbon-carbon double bond ($C = C$).



(b) Aryl halides

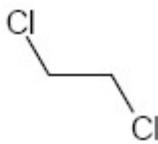
These are the compounds in which the halogen atom is bonded to the sp^2 -hybridised carbon atom of an aromatic ring.



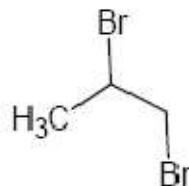
4.) Dihaloalkanes

(a) Vicinal dihalides

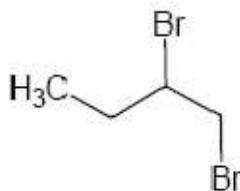
Contain both halogens on adjacent carbon atoms. Their common name is **Alkylene Dihalides**.



Ethylene Dichloride



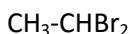
Propylene Dibromide



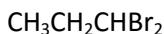
Butylene dibromide

(b) Gem dihalides

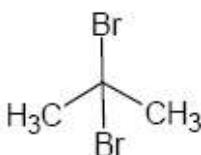
The two halogens are present on the same carbon atom.
Their common name is **Alkylidene Dihalides**.



Ethyldiene Dibromide



n-propylidene dibromide



Isopropylidene dibromide

5.) Trihaloalkanes



Chloroform



Bromoform



Iodoform



Fluoroform

6.) Tetrahaloalkanes

CCl_4 Carbom tetrachloride (Pyrene)
 {Tetrachloromethane}

6.) Polyhaloalkanes

C_2Cl_6 Hexachloroethane

Nomenclature

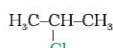
The common names of alkyl halides are derived by naming the alkyl group followed by the halide. Alkyl halides are named as halosubstituted hydrocarbons in the IUPAC system of nomenclature. Haloarenes are the common as well as IUPAC names of aryl halides. For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used.



Common name: n-Propyl bromide
IUPAC name: 1-Bromopropane



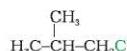
Common name: Bromobenzene
IUPAC name: Bromobenzene



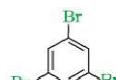
Isopropyl chloride
2-Chloropropane



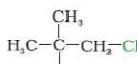
m-Dibromobenzene
1,3-Dibromobenzene



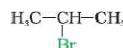
Isobutyl chloride
1-Chloro-2-methylpropane



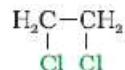
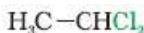
sym-Tribromobenzene
1,3,5-Tribromobenzene



IUPAC name: 1-Chloro-2,2-dimethylpropane



2-Bromopropane



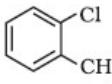
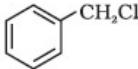
Common name: Ethyldene chloride
(*gem*-dihalide)

Ethylene dichloride
(*vic*-dihalide)

IUPAC name: 1, 1-Dichloroethane

1, 2-Dichloroethane

Table : Common and IUPAC names of some Halogen Compounds

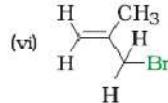
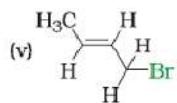
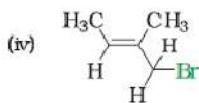
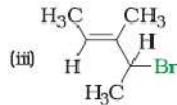
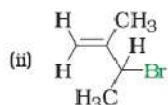
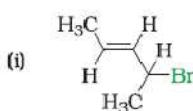
Structure	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	sec-Butyl chloride	2-Chlorobutane
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(\text{CH}_3)_3\text{CBr}$	tert-Butyl bromide	2-Bromo-2-methylpropane
$\text{CH}_2 = \text{CHCl}$	Vinyl chloride	Chloroethene
$\text{CH}_2 = \text{CHCH}_2\text{Br}$	Allyl bromide	3-Bromopropene
	<i>o</i> -Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
CHCl_3	Chloroform	Trichloromethane
CHBr_3	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	n-Propyl fluoride	1-Fluoropropane

Q. Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

(NCERT)

Q. Write IUPAC names of the following:

(NCERT)



Q Write structures of the following compounds:

- (i) 2-Chloro-3-methylpentane
- (ii) 1-Chloro-4-ethylcyclohexane
- (iii) 4-tert. Butyl-3-iodoheptane
- (iv) 1,4-Dibromobut-2-ene
- (v) 1-Bromo-4-sec. butyl-2-methylbenzene.

Nature of C-X Bond

Since halogen atoms are more electronegative than carbon, the carbonhalogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.

Since the size of halogen atom increases as we go down the group in the periodic table, fluorine atom is the smallest and iodine atom, the largest. Consequently the carbon-halogen bond length also increases from C—F to C—I.

Bond	Bond length/pm	C-X Bond enthalpies/ kJmol ⁻¹	Dipole moment/Dcbyc
CH ₃ -F	139	452	1.847
CH ₃ -Cl	178	351	1.860
CH ₃ -Br	193	293	1.830
CH ₃ -I	214	234	1.636

Physical Properties Boiling Point

- Because of their greater molecular weights, haloalkanes have considerably higher boiling points than alkanes with the same number of carbons.
- For a given alkyl group, the boiling point increases with increasing atomic weight of the halogen, so that a fluoride is the lowest boiling, an Iodide the highest boiling.
- For a given halogen, the boiling point rises with increasing carbon number. The boiling point rise is 20-30 degrees for each added carbon.
- Branching involving either the alkyl groups or the halogen itself –lowers the boiling point.

Solubility

- The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

Q. Arrange each set of compounds in order of increasing boiling points. NCERT

- (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
- (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

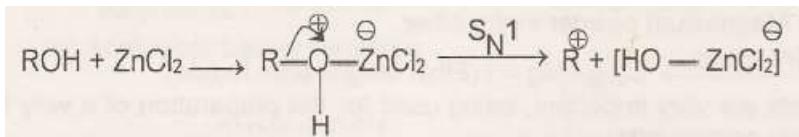
Methods of Preparation

1. Grove's process: *Reaction of alcohol with Lucas Reagent: (conc. HCl + anhyd. ZnCl)*

This reaction is used to test pri, sec, & tert alcohol. 30 alcohols reacts instantaneously & give turbidity due to formation of insoluble chloride. 2° alcohols react to give turbidity after 5 min. whereas 1° alcohols give no turbidity as there is no reaction at room temperature.

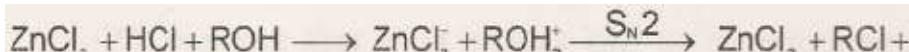
This test is applicable only for lower alcohols which are water soluble. It is because alcohols having more than 6 carbon are almost insoluble in water hence two immiscible liquid is present before the addition of Lucas Reagent, so the presence of alkyl halide can't be detected properly.

In this process replacement "OH" group in primary and secondary alcohols with an "X" atom by means of Hydrogen chloride or bromide in presence of Zinc chloride. But for tertiary alcohol readily react with concentrated hydrochloric acid in the absence of zinc chloride. Zinc chloride is a lewis acid and consequently can co-ordinate with the alcohol



The R-O bond is weakened and so the complex readily forms a carbonium ion ($\text{S}_{\text{N}}1$ mechanism). If the nature of R^+ is such that it can undergo rearrangement the product will be mixture of isomeric alkyl chlorides.

The reaction also follows $\text{S}_{\text{N}}2$ mechanism when the concentration of zinc chloride is low, the reaction is still

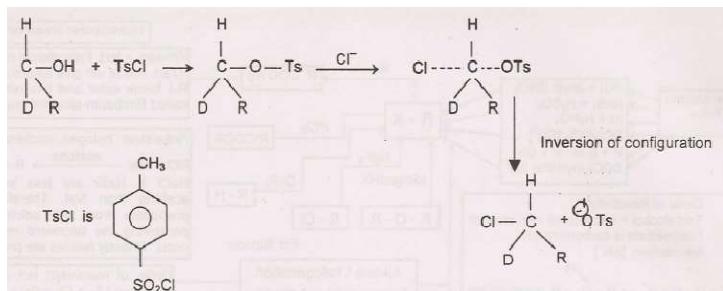


- Pyridine and dimethyl amine also catalyse the reaction between alcohols and hydrochloric acid without rearrangement

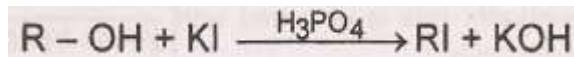
To avoid rearrangement or to make this reaction $\text{S}_{\text{N}}2$.

Tosylation process can be used, - OTs

is a weak nucleophile & better leaving group. Due to its bulkiness it prefers $\text{S}_{\text{N}}2$ reaction by backside attack of nucleophile.



- $\text{R-OH} + \text{NaBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{R-Br} + \text{NaI}$
- For alkyl iodide a non oxidising acid is used along with KI [HI is not preferred as it is a good reducing agent]

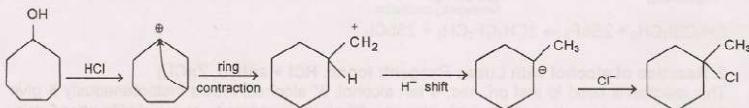
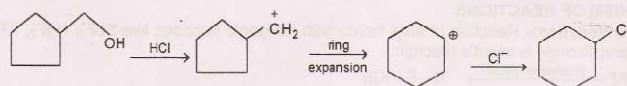
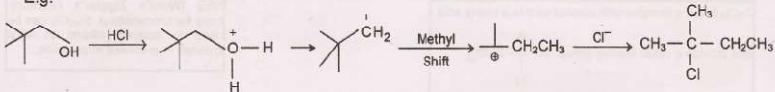


Q. Why is sulphuric acid not used during the reaction of alcohols with KI? **(NCERT)**

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Q. What happens when neopentyl alcohol reacts with anhydrous hydrogen bromide?

E.g.

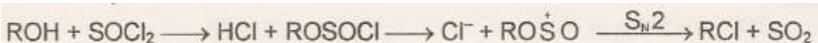


Ring expansion will take place if ring size is (4 or 5 membered) & positive charge present on carbon atom directly attached to the ring (note: In C_6H_9^+ ring expansion will not be preferred as this carbocation is stable due to bent bond overlapping)

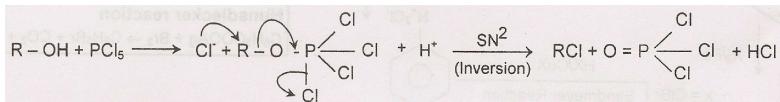
Ring contraction will take place if ring is larger than 6 membered & positive charge should be present on the ring.

2. Darzen's Process. Thionyl chloride reacts with straight-chain primary alcohols without rearrangement in the presence or absence of pyridine the reaction proceeds via a chloro sulphite

Mechanism



3. With PCl_5

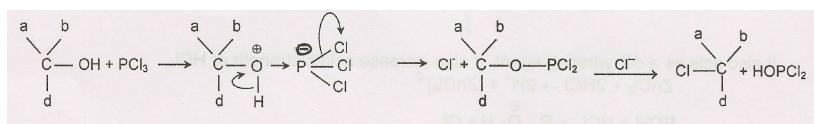


If R group is tertiary, It will be $\text{S}_{\text{N}}1$ reaction which takes place via recamization (via carbocation formation). Rearrangement also takes place.

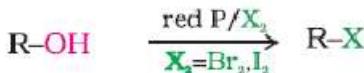
4. Reaction with phosphorus Halide.

This reaction takes place via $\text{SN}2$ without rearrangement and via inversion of configuration.

[Only with 3° alcohol reaction is $\text{SN}1$ & nucleophile can attack from either ends on carbocation to give a racemic mixture].



Phosphorus tribromide and triiodide are usually generated *in situ* (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine respectively.



5. By Free Radical Halogenation

Detailed Mechanism (Free radical Substitution Reaction)

1. Initiation Step

It is the hemolytic cleavage of chlorine molecule to chlorine free radical by absorbing energy when Cl_2 is subjected to UV light at room temperature.

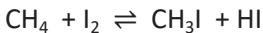
2. Propagation step

- The chlorine free radical attacks the alkane molecule , abstracts a hydrogen atom giving hydrogen chloride and alkyl free radical.
- The alkyl free radical reacts further with a chlorine molecule forming alkyl chloride and chlorine free radical.

3. Termination Step.

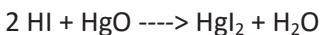
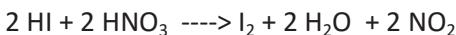
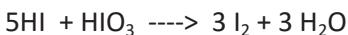
In this step , the free radicals obtained during the propagation may combine to give products.

- Iodination of alkanes is slow and reversible process because of formation of strong reducing agent , hydrogen iodide , as a by- product which reduces iodoalkane back to alkane



Thus direct iodination of alkane is not possible.

To get iododerivatives we use strong oxidizing agents like iodic acid (HIO_3) ,periodic acid (HIO_4) , nitric acid (HNO_3) or mercuric oxide HgO which convert HI to I_2 or destroy Iodide



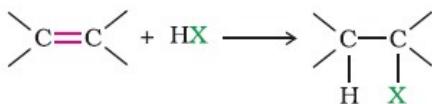
- Fluorination of alkanes is highly exothermic or explosive, hence it cannot be controlled under ordinary conditions. Further more , fluorination brings about extensive rupture of C-C and C-H bond leading to a mixture of fluoroproducts.

Q. Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $(CH_3)_2CHCH_2CH_3$.

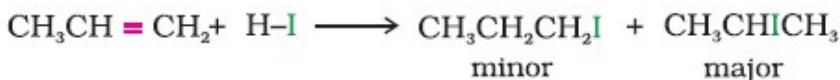
(NCERT)

6.) From alkenes

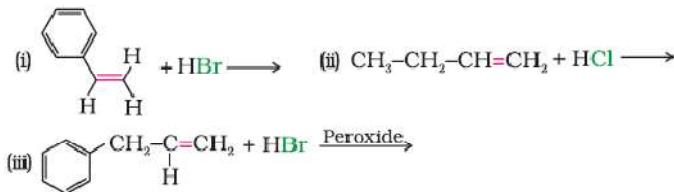
(i) **Addition of hydrogen halides:** An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.



Propene yields two products, however only one predominates as per Markovnikov's rule.



Q. Write the products of the following reactions:



7.) Halogen exchange

a) Finkelstein Reaction

Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in **dry acetone**.



NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

b) Swarts Reaction

The synthesis of alkyl fluorides is done by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg₂F₂, CoF₂ or SbF₃.



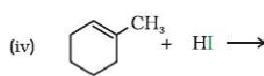
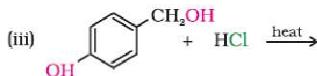
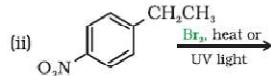
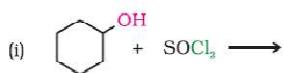
Q. Write structures of different dihalogen derivatives of propane.
NCERT

Q. Among the isomeric alkanes of molecular formula C₅H₁₂, identify the one that on photochemical chlorination yields

NCERT

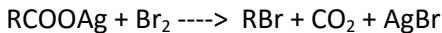
- (i) A single monochloride.
- (ii) Three isomeric monochlorides.
- (iii) Four isomeric monochlorides.

Q. Draw the structures of major monohalo products in each of the following reactions:



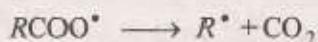
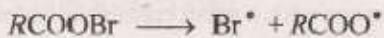
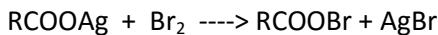
NCERT

8.) Borodine Hundsdiecker reaction



The yield of halide is primary > secondary > tertiary

Mechanism is through free radical formation:



Reactions of Haloalkanes

(i) Nucleophilic substitution reactions

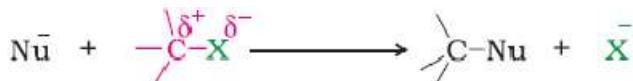


Table : Nucleophilic Substitution of Alkyl Halides (R-X)
 $\text{R-X} + \text{Nu}^- \rightarrow \text{R-Nu} + \text{X}^-$

Reagent	Nucleophile (Nu ⁻)	Substitution product R-Nu	Class of produ
NaOH (KOH)	HO ⁻	ROH	Alcohol
H ₂ O	H ₂ O	ROH	Alcohol
NaOR'	R'O ⁻	ROR'	Ether
Ial	I ⁻	R—I	Alkyl i
NH ₃	NH ₃	RNH ₂	Primar
R'NH ₂	R'NH ₂	RNHR'	Sec. a
R'R''NH	R'R''H	RNR'R''	Tert. a
KCN	—C≡N:	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitr
KNO ₂	O=N—O	R—O—N=O	Alkyl i
AgNO ₂	Ag—O—N=O	R—NO ₂	Nitroa
R'COOAg	R'COO ⁻	R'COOR	Ester
LiAlH ₄	H	RH	Hydro
R'-M [*]	R'	RR'	Alkanes

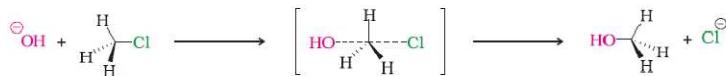
Groups like cyanides and nitrites possess two nucleophilic centres and are called ***ambident nucleophiles***. Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways [$\text{C}\equiv\text{N} \leftrightarrow :\text{C}=\text{N}^-$], i.e., linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage [$-\text{O}-\text{N}=\text{O}$]. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

Q. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

(NCERT)

KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

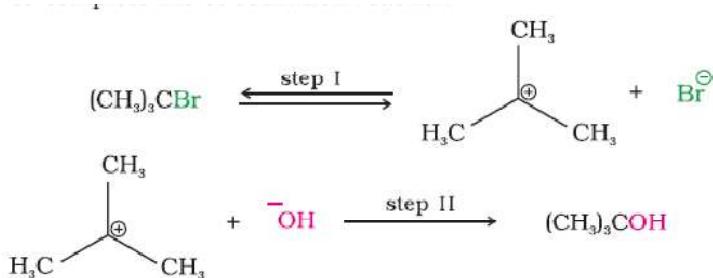
(a) Substitution nucleophilic bimolecular (S_N2)



The incoming nucleophile interacts with alkyl halide causing the carbon-halide 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. As the reaction progresses and the bond between the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. As this happens, the configuration of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind, while the leaving group is pushed away. This process is called as **inversion of configuration**. In the transition state, the carbon atom is simultaneously bonded to incoming nucleophile and the outgoing leaving group and such structures are unstable and cannot be isolated. This is because the carbon atom in the transition state is simultaneously bonded to five atoms and therefore is unstable. Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus the order of reactivity followed is:

Primary halide > Secondary halide > Tertiary halide.

(b) Substitution nucleophilic unimolecular (S_N1)



It occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction. Step I is the slowest and reversible. It involves the C—Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion. Further, greater the stability of carbocation, greater will be its ease of formation from alkyl halides, 3° alkyl halides undergo S_N1 reaction very fast because of the high stability of 3° carbocations.

For S_N2 reaction

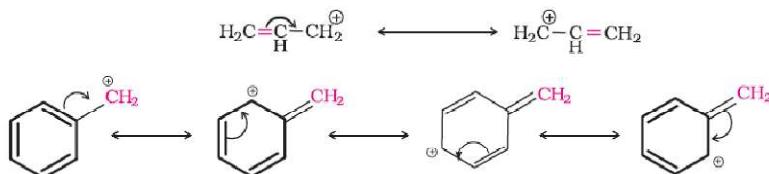


Tertiary halide; Secondary halide; Primary halide; CH₃X



For S_N1 reaction

Allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance



For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms R-I > R-

Br

In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?

Q

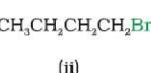
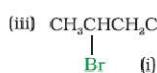
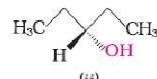
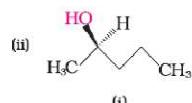
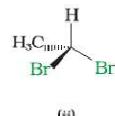
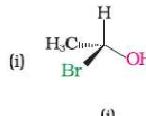


Q. Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

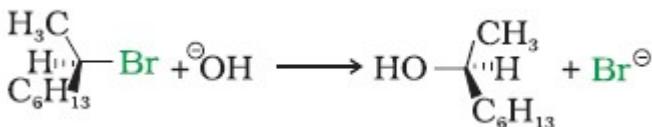
(i) The four isomeric bromobutanes

(ii) C₆H₅CH₂Br, C₆H₅CH(C₆H₅)Br, C₆H₅CH(CH₃)Br, C₆H₅C(CH₃)(C₆H₅)Br

Q. Identify chiral and achiral molecules in each of the following pair of compounds.



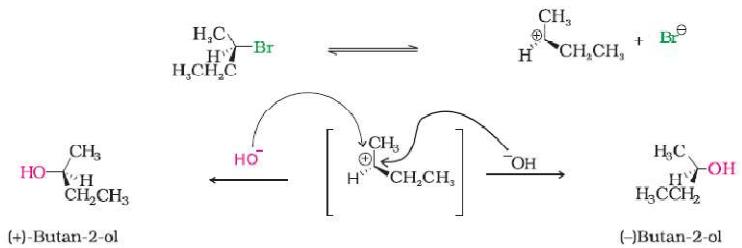
In case of optically active alkyl halides, the product formed as a result of SN2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. When (-)-2-bromo-octane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied.



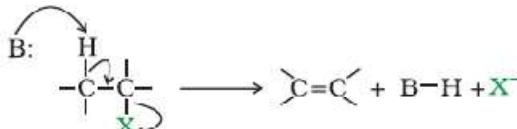
Thus, SN2 reactions of optically active halides are accompanied by inversion of configuration.

In case of optically active alkyl halides, SN1 reactions are accompanied by racemisation. Actually the carbocation formed in the slow step being *sp*2 hybridised is planar (achiral). The attack of the nucleophile may be accomplished from either side resulting in a mixture of products, one having the same configuration (the –OH attaching on the same position as halide ion) and the other having opposite configuration (the –OH attaching on the side opposite to halide ion). This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (\pm)-butan-2-ol.

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2. Elimination reactions

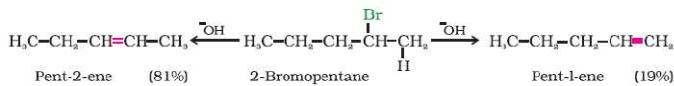


B=Base ; X=Leaving group

Saytzeff Rule

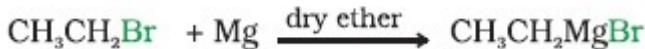
“in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.”

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



3. Reaction with metals

Grignard Reagents.



These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons.



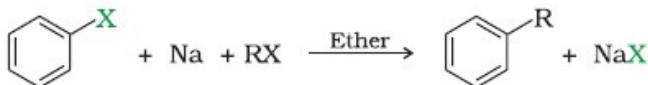
Wurtz reaction

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



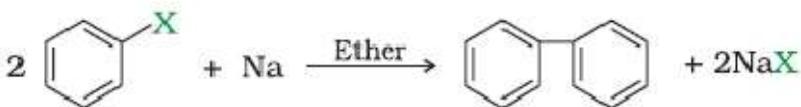
Wurtz-Fittig reaction

A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.



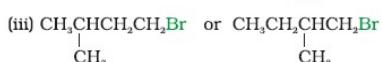
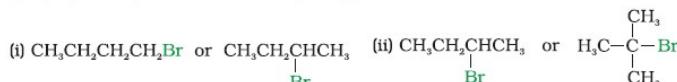
Fittig reaction

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.



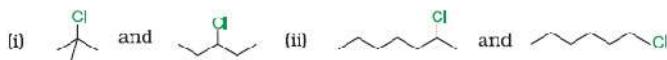
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Q. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.



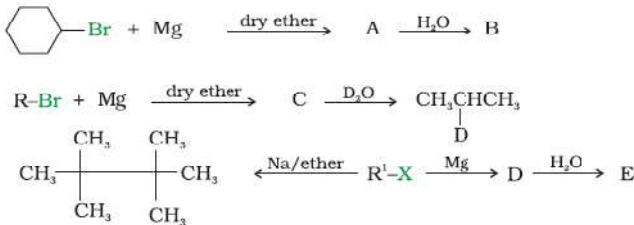
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Q. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?



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Q. Identify A, B, C, D, E, R and R¹ in the following:

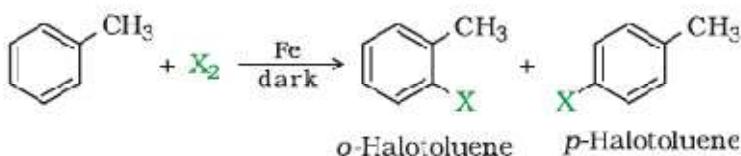


Aryl Halides

Methods of Preparation

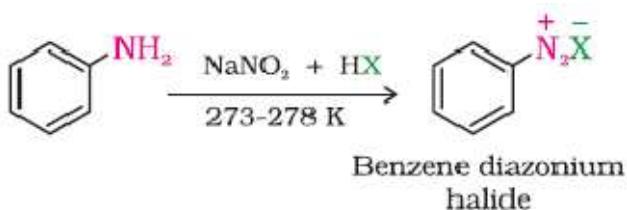
a) By electrophilic substitution

Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride. The *ortho* and *para* isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO₃, HIO₄) to oxidise the HI formed during iodination.

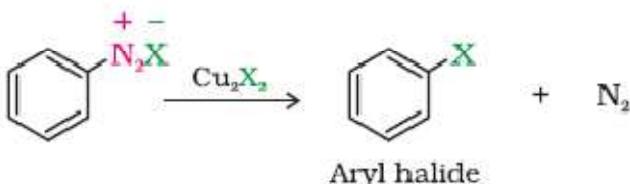


(b) Sandmeyer's reaction

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br.

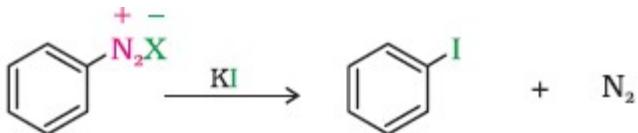


Benzene diazonium
halide



Aryl halide

Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.

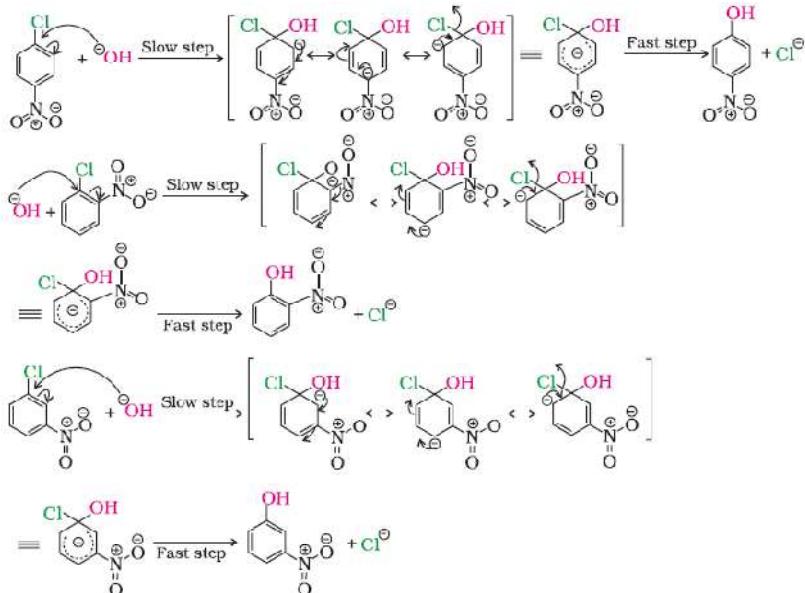


Reactions of Haloarenes

Aryl halides are extremely less reactive towards nucleophilic substitution reactions

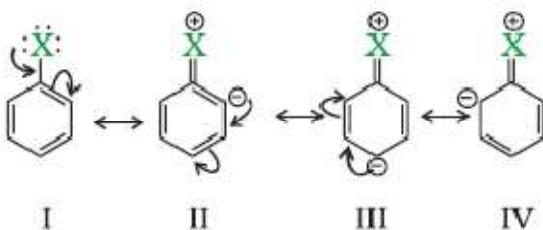
The presence of an electron withdrawing group ($-NO_2$) at *ortho*- and *para*-positions increases the reactivity of haloarenes.

The effect is pronounced when ($-NO_2$) group is introduced at *ortho* and *para*- positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at *meta*-position. Mechanism of the reaction is as depicted:



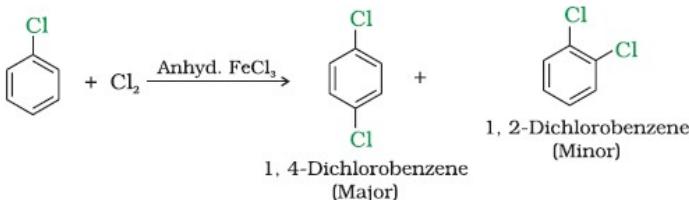
2. Electrophilic substitution reactions

Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is *o*, *p*directing; therefore, further substitution occurs at *ortho*- and *para*positions with respect to the halogen atom. The *o*, *p*-directing influence of halogen atom can be easily understood if we consider the resonating structures of halobenzene

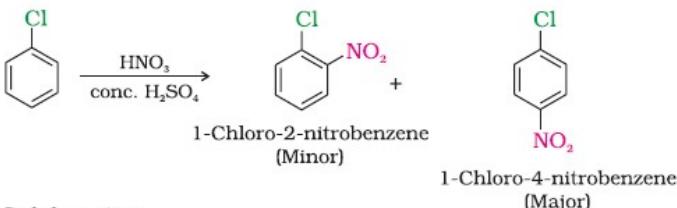


Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. Further, the halogen atom because of its $-I$ effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

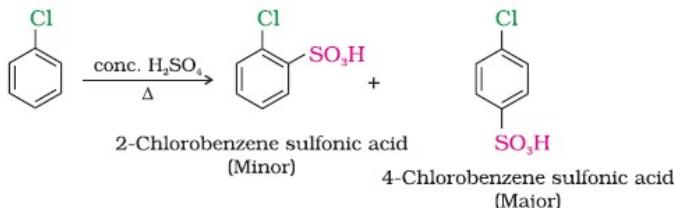
(i) Halogenation



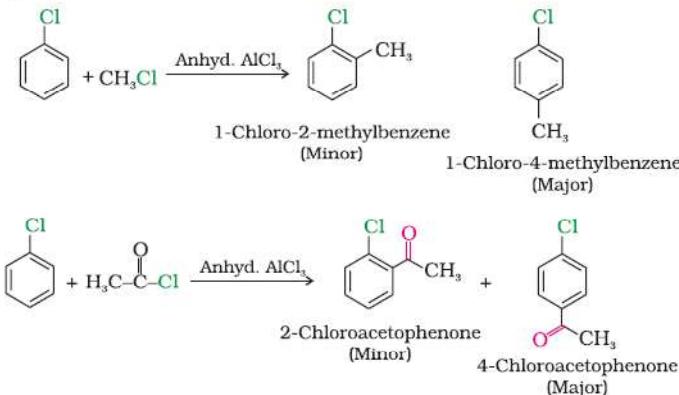
(ii) Nitration



(iii) Sulphonation



(iv) Friedel-Crafts reaction



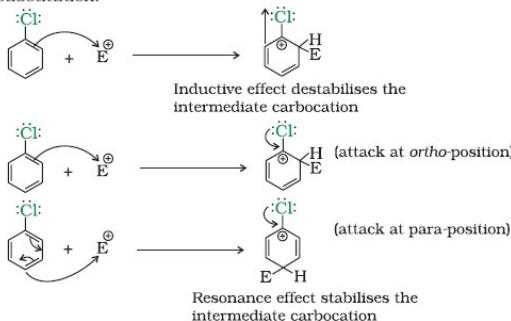
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Example

Although chlorine is an electron withdrawing group, yet it is *ortho*-*para*- directing in electrophilic aromatic substitution reactions. Why?

Solution

Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.



Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para* positions and hence makes the deactivation less for *ortho*- and *para* attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

NCERT Exercise

Q1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

- | | |
|-----------------------------------|-------------------------------------|
| (i) $(CH_3)_2CHCH(Cl)CH_3$ | (ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$ |
| (iii) $CH_3CH_2C(CH_3)_2CH_2I$ | (iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$ |
| (v) $CH_3CH(CH_3)CH(Br)CH_3$ | (vi) $CH_3C(C_2H_5)_2CH_2Br$ |
| (vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$ | (viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$ |
| (ix) $CH_3CH=CHC(Br)(CH_3)_2$ | (x) $p-CIC_6H_4CH_2CH(CH_3)_2$ |
| (xi) $m-CIC_6H_4CH_2C(CH_3)_3$ | (xii) $o-Br-C_6H_4CH(CH_3)CH_2CH_3$ |

Q2 Give the IUPAC names of the following compounds:

- (i) $CH_3CH(Cl)CH(Br)CH_3$ (ii) $CHF_2CBrClF$ (iii) $CICH_2C\equiv CCH_2Br$
(iv) $(CCl_3)_3CCl$ (v) $CH_3C(p-CIC_6H_4)_2CH(Br)CH_3$ (vi) $(CH_3)_3CCH=CIC_6H_4I-p$

Q3 Write the structures of the following organic halogen compounds.

- | | |
|---|--------------------------------------|
| (i) 2-Chloro-3-methylpentane | (ii) <i>p</i> -Bromochlorobenzene |
| (iii) 1-Chloro-4-ethylcyclohexane | (iv) 2-(2-Chlorophenyl)-1-iodooctane |
| (v) Perfluorobenzene | (vi) 4-tert-Butyl-3-iodoheptane |
| [vii] 1-Bromo-4-sec-butyl-2-methylbenzene | [viii] 1,4-Dibromobut-2-ene |

Q 4 Which one of the following has the highest dipole moment?

- (i) CH_2Cl_2 (ii) CHCl_3 (iii) CCl_4

Q 5 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

Q.6 Write the isomers of the compound having formula C_4H_9Br .

Q.7 Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.

Q.8 What are ambident nucleophiles? Explain with an example.

Q.9 Which compound in each of the following pairs will react faster in SN₂ reaction

with –OH?

- (i) CH₃Br or CH₃I (ii) (CH₃)₃CCl or CH₃Cl

Q.10 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-

methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

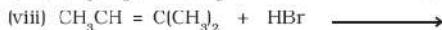
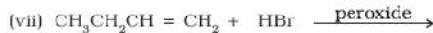
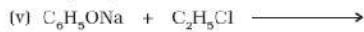
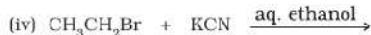
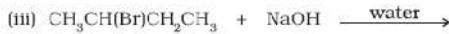
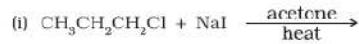
Q.11 How will you bring about the following conversions?

- (i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii)
Propene to
1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to
propyne
(vi) Ethanol to ethyl fluoride (vii) Bromomethane to
propanone (viii) But-1-ene
to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to
biphenyl.

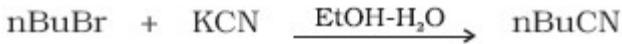
Q.12 Explain why

- (i) the dipole moment of chlorobenzene is lower than that of
cyclohexyl chloride?
(ii) alkyl halides, though polar, are immiscible with water?
(iii) Grignard reagents should be prepared under anhydrous
conditions?

Q. 1.4 Write the structure of the major organic product in each of the following reactions:



Q.15 Write the mechanism of the following reaction:



Q 16 Arrange the compounds of each set in order of reactivity towards SN₂ displacement:

- (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
- (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane
- (iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

Q.17 Out of C₆H₅CH₂Cl and C₆H₅CHClC₆H₅, which is more easily hydrolysed by aqueous KOH?

Q.18 *p*-Dichlorobenzene has higher m.p. and solubility than those of *o*- and *m*-isomers.

Discuss.

Q.19 How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) Ethanol to but-1-yne

iii) 1-Bromopropane to 2-bromopropane

(iv) Toluene to benzyl alcohol

(v) Benzene to 4-bromonitrobenzene

(vi) Benzyl alcohol to 2-phenylethanoic acid

(vii) Ethanol to propanenitrile

(viii) Aniline to chlorobenzene

(ix) 2-Chlorobutane to 3, 4-dimethylhexane

(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane

(xi) Ethyl chloride to propanoic acid

(xii) But-1-ene to n-butyliodide

(xiii) 2-Chloropropane to 1-propanol

(xiv) Isopropyl alcohol to iodoform

(xv) Chlorobenzene to *p*-nitrophenol

(xvi) 2-Bromopropane to 1-bromopropane

(xvii) Chloroethane to butane

(xviii) Benzene to diphenyl

(xix) *tert*-Butyl bromide to isobutyl bromide

(xx) Aniline to phenylisocyanide

Q.20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Q.21 Primary alkyl halide C₄H₉Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C₈H₁₈ which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

Q.22 What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

(vi) methyl chloride is treated with KCN?

Alcohols

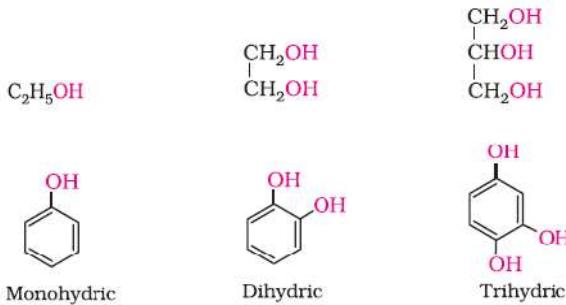
Alcohols and **phenols** are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group.

The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group ($R-O/Ar-O$) yields another class of compounds known as '**ethers**'

Classification

Mono, Di, Tri or Polyhydric Compounds

Alcohols and phenols may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups



(i) *Compounds containing $C_{sp^3}-OH$ bond:*

In this class of alcohols, the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows:

Primary, secondary and tertiary alcohols: In these three types of alcohols, the —OH group is attached to primary, secondary and tertiary carbon atom.



Primary (1°)



Secondary (2°)



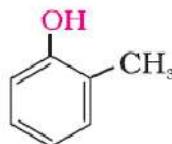
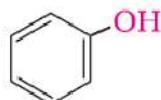
Tertiary (3°)

(i) *Compounds containing C_{sp^2} —OH bond:*

These alcohols contain —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols.

Vinylic alcohol: $\text{CH}_2 = \text{CH} - \text{OH}$

Phenols:

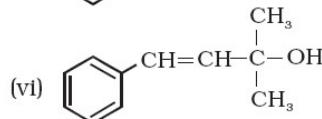
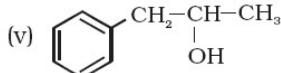
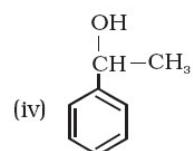
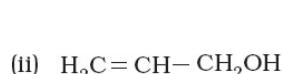
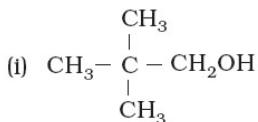


Ethers

Ethers are classified as **simple** or **symmetrical**, if the alkyl or aryl groups attached to the oxygen atom are the same, and **mixed** or **unsymmetrical**, if the two groups are different.

Diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, is a symmetrical ether whereas $\text{C}_2\text{H}_5\text{OCH}_3$ and $\text{C}_2\text{H}_5\text{OC}_6\text{H}_5$ are unsymmetrical ethers.

Q. Classify the following as primary, secondary and tertiary alcohols:



Identify allylic alcohols in the above examples.

Nomenclature

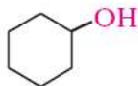
(a) *Alcohols:* The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. For example, CH₃OH is methyl alcohol.

Table 11.1: Common and IUPAC names of some Alcohols

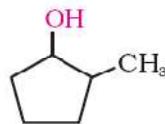
Compound	Common name	IUPAC name
CH ₃ – OH	Methyl alcohol	Methanol
CH ₃ – CH ₂ – CH ₂ – OH	<i>n</i> -Propyl alcohol	Propan-1-ol
CH ₃ – CH – CH ₃ OH	Isopropyl alcohol	Propan-2-ol
CH ₃ – CH ₂ – CH ₂ – CH ₂ – OH	<i>n</i> -Butyl alcohol	Butan-1-ol
CH ₃ – CH – CH ₂ – CH ₃ OH	<i>sec</i> -Butyl alcohol	Butan-2-ol
CH ₃ – CH – CH ₂ – CH ₃ OH	Isobutyl alcohol	2-Methylpropan-1-ol
CH ₃ – C – OH CH ₃	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
CH ₂ – CH – CH ₂ OH OH OH	Glycerol	Propane -1, 2, 3-triol

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Cyclic alcohols are named using the prefix cyclo and considering the —OH group attached to C-1.



Cyclohexanol



2-Methylcyclopentanol

(b) Phenols:



Common name
IUPAC name

Phenol
Phenol



o-Cresol
2-Methylphenol



m-Cresol
3-Methylphenol



p-Cresol
4-Methylphenol

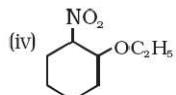
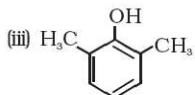
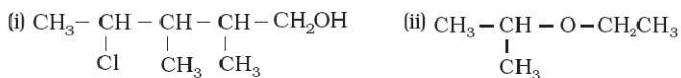
(c) Ethers:

Table Common and IUPAC names of some Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6 - \text{CH}_3$	Heptylphenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}-\text{CH}-\text{CH}_3$ $\quad\quad\quad\text{CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_3$	Phenylisopentyl ether	3- Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethyleyclohexane

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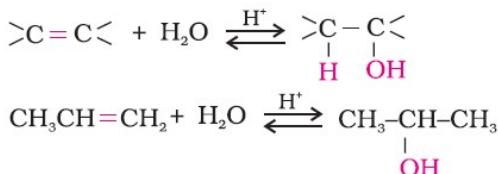
Q. Give IUPAC names of the following compounds:



Preparation of Alcohols

1. From alkenes

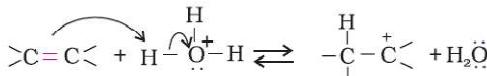
(i) *By acid catalysed hydration:* Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule



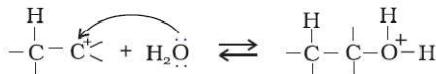
Mechanism

The mechanism of the reaction involves the following three steps:

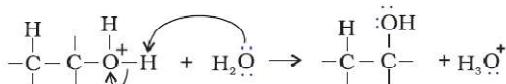
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



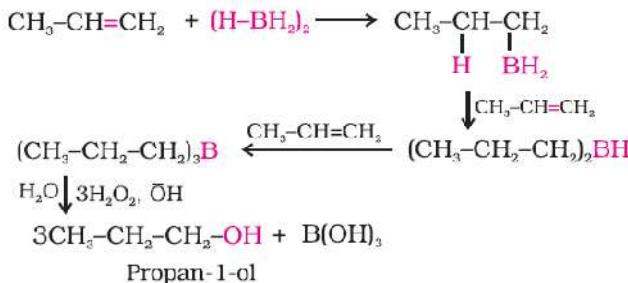
Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.



(ii) By hydroboration–oxidation: Diborane (BH_3H_2) reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

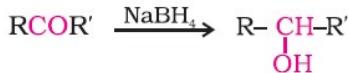


The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the sp^2 carbon carrying greater number of hydrogen atoms. The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule.

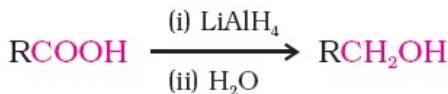
2. From carbonyl compounds

(i) By reduction of aldehydes and ketones: Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation). The usual catalyst is a finely divided metal such as platinum, palladium or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride (NaBH_4) or lithium

aluminium hydride (LiAlH_4).



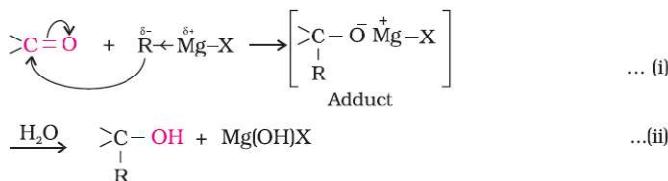
(ii) *By reduction of carboxylic acids and esters:* Carboxylic acids are reduced to primary alcohols in excellent yields by lithium aluminium hydride, a strong reducing agent.



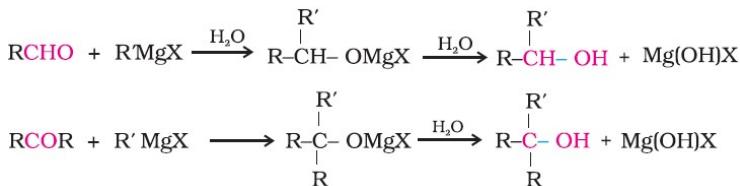
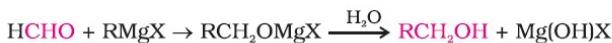
3. From Grignard reagents

Alcohols are produced by the reaction of Grignard reagents with aldehydes and ketones. The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct.

Hydrolysis of the adduct yields an alcohol.



The overall reactions using different aldehydes and ketones are as follows:



Q

Give the structures and IUPAC names of the products expected from the following reactions:

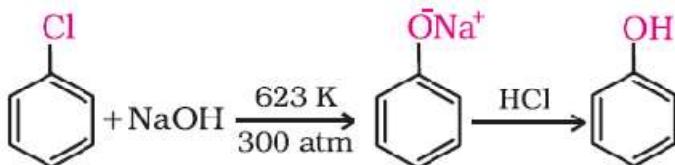
- (a) Catalytic reduction of butanal.
- (b) Hydration of propene in the presence of dilute sulphuric acid.
- (c) Reaction of propanone with methylmagnesium bromide followed by hydrolysis.

CH₃

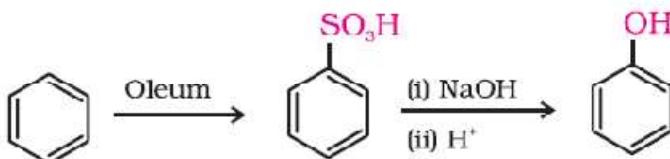
(NCERT)

Preparation of Phenols

1. From haloarenes



2. From benzenesulphonic acid



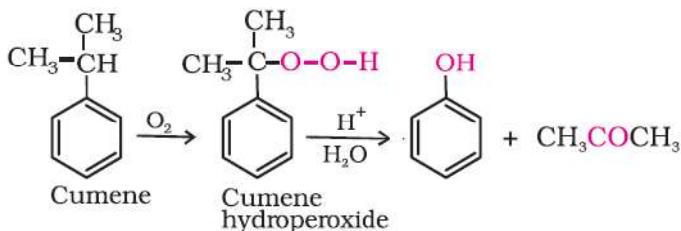
3. From diazonium salts



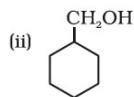
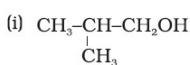
4. From cumene

Phenol is manufactured from the hydrocarbon, cumene.

Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid.

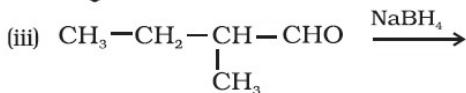
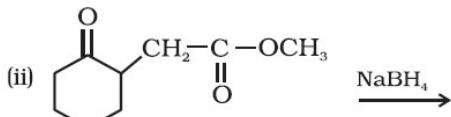
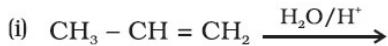


Q Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?



(NCERT)

Q Write structures of the products of the following reactions:



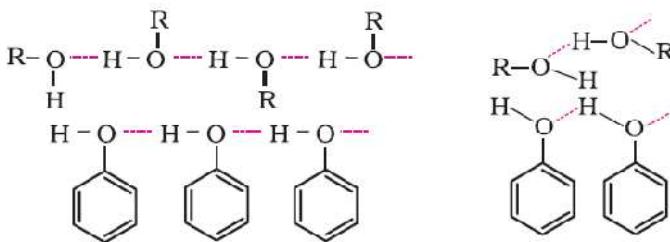
(NCERT)

Physical Properties

Boiling Points

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.



Solubility

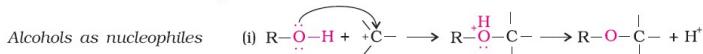
Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups. Several of the lower molecular mass alcohols are miscible with water in all proportions.

- Q** Arrange the following sets of compounds in order of their increasing boiling points:
- (a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.
 - (b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

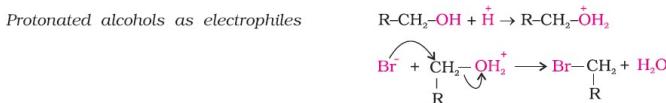
(NCERT)

Chemical Reactions

Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O–H is broken when alcohols react as nucleophiles.



(ii) The bond between C–O is broken when they react as electrophiles. Protonated alcohols react in this manner.



Based on the cleavage of O–H and C–O bonds, the reactions of alcohols and phenols may be divided into two groups:

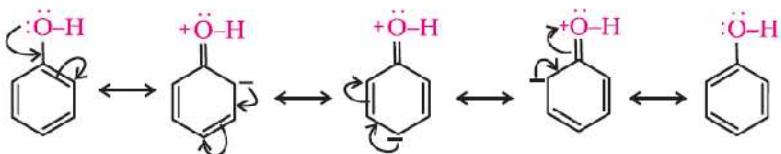
(a) Reactions involving cleavage of O–H bond

1. Acidity of alcohols and phenols

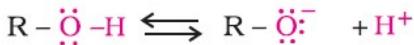
(i) *Acidity of alcohols*: The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O–H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



(ii) Acidity of phenols: The hydroxyl group, in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.



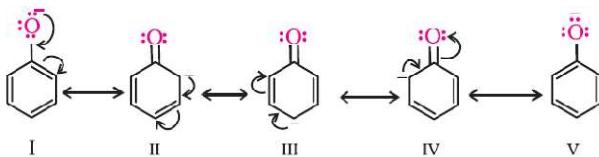
Phenols are stronger acids than alcohols and water.



Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of O–H bond and results in an increase in ionisation of phenols than that of alcohols.

Alkoxide and phenoxide ions

In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.



In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other

hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

Table : pK_a Values of some Phenols and Ethanol

Compound	Formula	pK_a
<i>o</i> -Nitrophenol	$o\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.2
<i>m</i> -Nitrophenol	$m\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	8.3
<i>p</i> -Nitrophenol	$p\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.1
Phenol	$\text{C}_6\text{H}_5\text{-OH}$	10.0
<i>o</i> -Cresol	$o\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
<i>m</i> -Cresol	$m\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.1
<i>p</i> -Cresol	$p\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	15.9

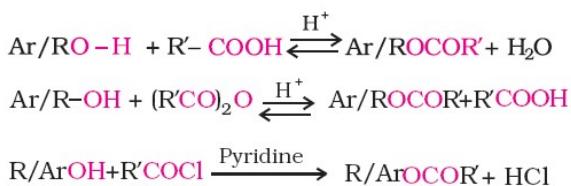
Q.

Arrange the following compounds in increasing order of their acid strength:
Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol,
phenol, 4-methylphenol.

(NCERT)

2. Esterification

Alcohols and phenols react with carboxylic acids, acid



The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



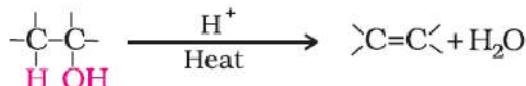
(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

1. Reaction with hydrogen halides:

2. Reaction with phosphorus trihalides:

3. Dehydration:

Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H_2SO_4 or H_3PO_4 , or catalysts such as anhydrous zinc chloride or alumina.

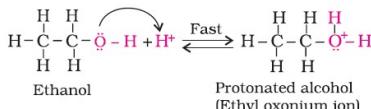


The relative ease of dehydration of alcohols follows the following order:

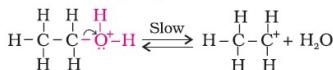
Tertiary > Secondary > Primary

Mechanism

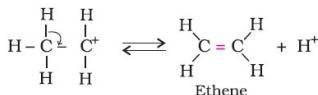
Step 1: Formation of protonated alcohol.



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



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



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

4. Oxidation:

Oxidation of alcohols involves the formation of a carbonoxygen double bond with cleavage of an O-H and C-H bonds.



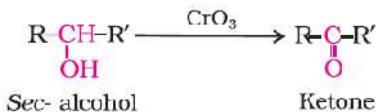
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.



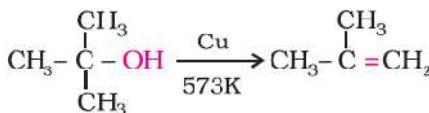
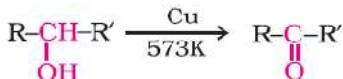
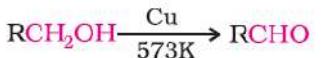
A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC).



Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).



When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.

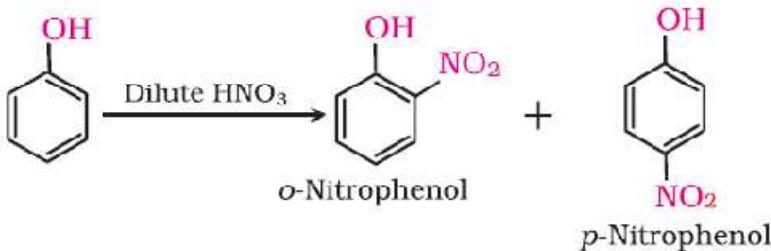


(c) Reactions of phenols

1. Electrophilic aromatic substitution

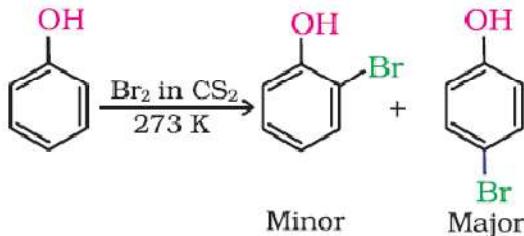
The $-OH$ group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect caused by $-OH$ group.

(i) *Nitration:* With dilute nitric acid at low temperature (298 K), phenol yields a mixture of *ortho* and *para* nitrophenols.

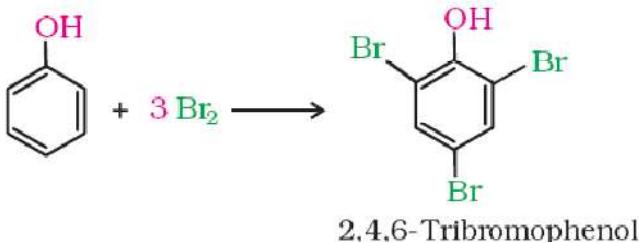


(ii) *Halogenation:* On treating phenol with bromine, different reaction products are formed under different experimental conditions.

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



(b) When phenol is treated with bromine water, 2,4,6-



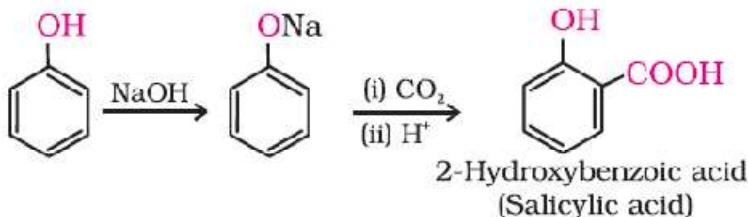
Q. Write the structures of the major products expected from the following reactions:

- (a) Mononitration of 3-methylphenol
- (b) Dinitration of 3-methylphenol
- (c) Mononitration of phenyl methanoate.

(NCERT)

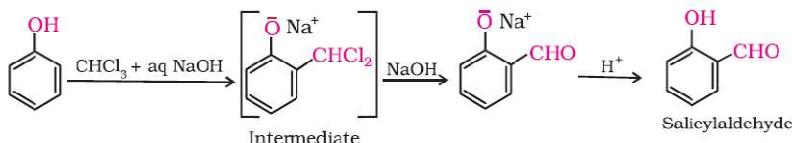
2. Kolbe's reaction

Phenoxyde ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.



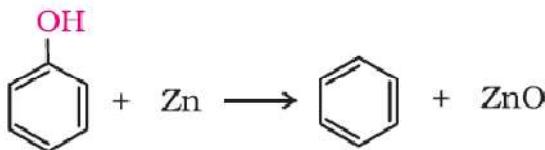
3. Reimer-Tiemann reaction

On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at *ortho* position of benzene ring. This reaction is known as *Reimer - Tiemann reaction*. The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



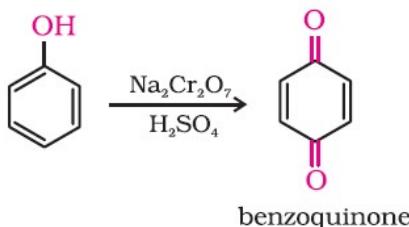
4. Reaction of phenol with zinc dust

Phenol is converted to benzene on heating with zinc dust.



5. Oxidation

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



(NCERT)

- Q.** Predict the major product of acid catalysed dehydration of
 (i) 1-methylcyclohexanol and (ii) butan-1-ol

(NCERT)

Q.

Ortho and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

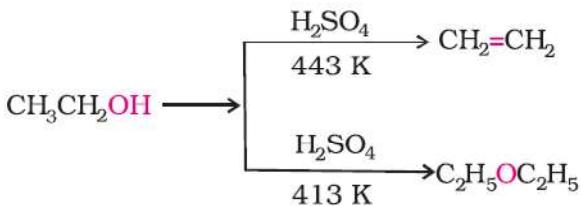
(NCERT)

Ethers

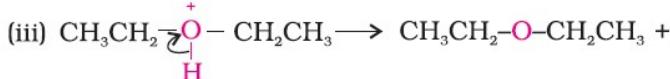
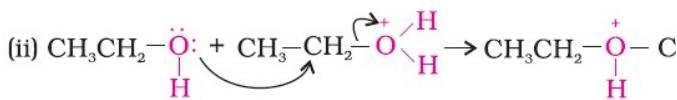
Preparation of Ethers

1. By dehydration of alcohols

Alcohols undergo dehydration in the presence of protic acids (H_2SO_4 , H_3PO_4). The formation of the reaction product, alkene or ether depends on the reaction conditions. For example, ethanol is dehydrated to ethene in the presence of sulphuric acid at 443 K. At 413 K, ethoxyethane is the main product.

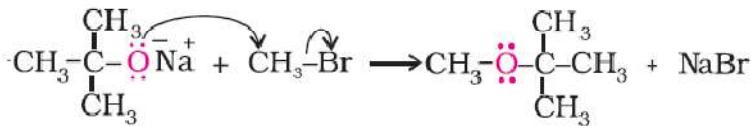


(SN2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

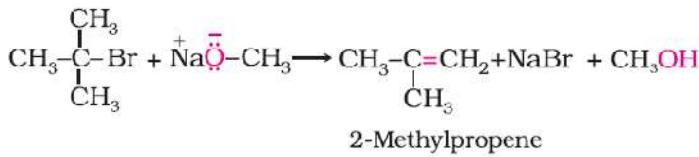


2. Williamson synthesis

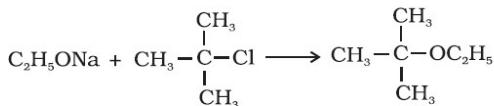
Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves SN2 attack of an alkoxide ion on primary alkyl halide.



Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH₃ONa with (CH₃)₃C—Br gives exclusively 2-methylpropene.



- Q. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.



- (i) What would be the major product of this reaction ?
(ii) Write a suitable reaction for the preparation of t-butylethyl ether.

(NCERT)

Physical Properties

The C-O bonds in ethers are polar and thus, ethers have a net dipole moment.

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

The miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule.

Chemical Reactions

1. Cleavage of C–O bond in ethers

Ethers are the least reactive of the functional groups. The cleavage of C–O bond in ethers takes place under drastic conditions with excess of hydrogen halides.

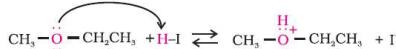
Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.



Mechanism

The reaction of an ether with concentrated HI starts with protonation of ether molecule.

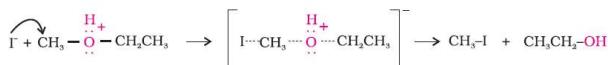
Step 1:



The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

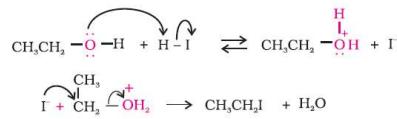
Step 2:

Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by S_N2 mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

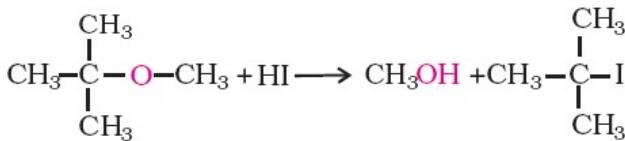


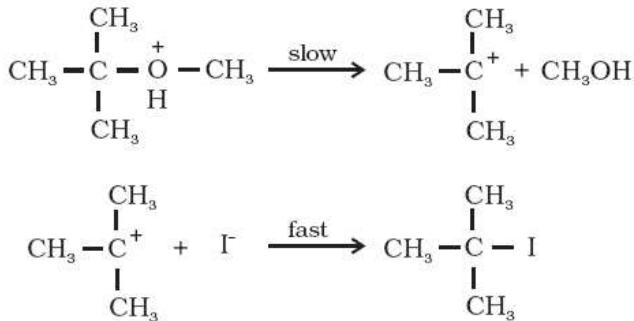
When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

Step 3:



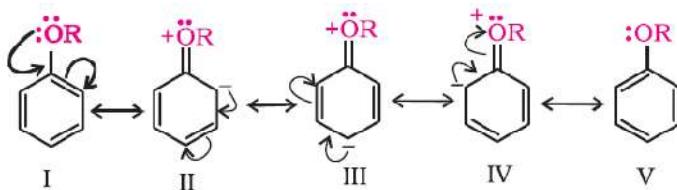
However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



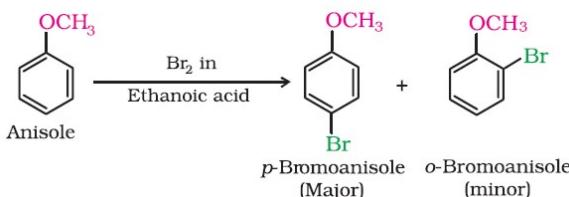


2. Electrophilic substitution

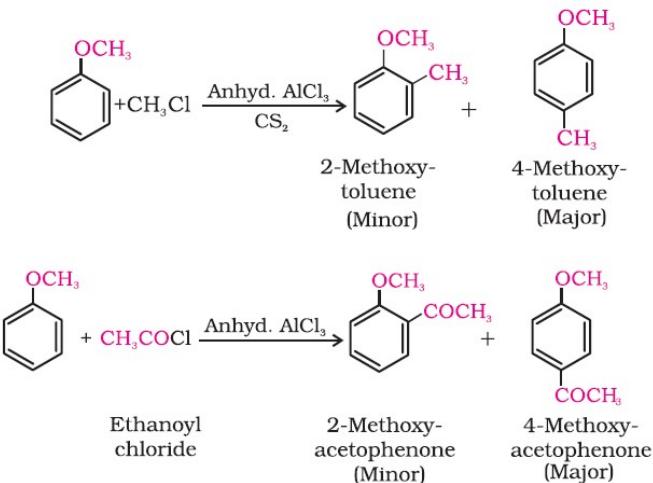
The alkoxy group (-OR) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.



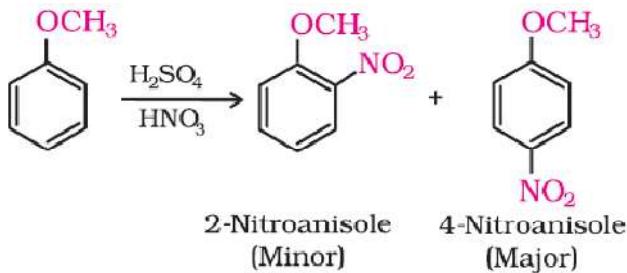
(i) Halogenation:



(ii) Friedel-Crafts reaction:



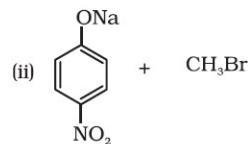
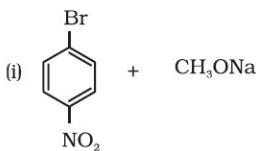
(iii) Nitration:



Q. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

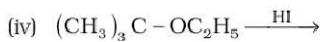
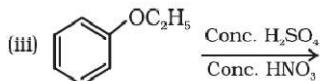
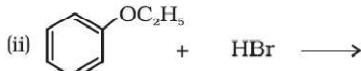
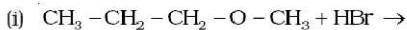
(NCERT)

Q. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



(NCERT)

Predict the products of the following reactions:

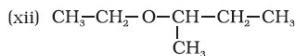
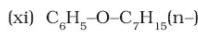
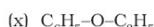
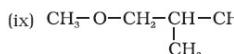
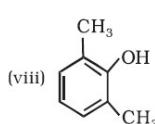
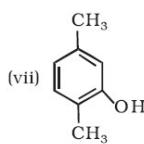
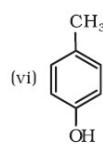
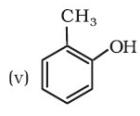
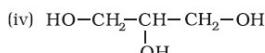
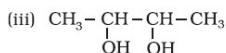
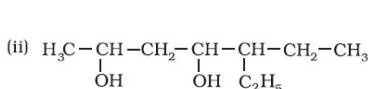
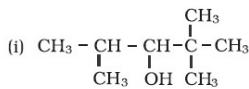


(NCERT)

NCERT Exercise

Q 1.

Write IUPAC names of the following compounds:



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Q. Write structures of the compounds whose IUPAC names are as follows:

- | | |
|---|--------------------------------|
| (i) 2-Methylbutan-2-ol | (ii) 1-Phenylpropan-2-ol |
| (iii) 3,5-Dimethylhexane -1, 3, 5-triol | (iv) 2,3 – Diethylphenol |
| (v) 1 – Ethoxypropane | (vi) 2-Ethoxy-3-methylpentane |
| (vii) Cyclohexylmethanol | (viii) 3-Cyclohexylpentan-3-ol |
| (ix) Cyclopent-3-en-1-ol | (x) 3-Chloromethylpentan-1-ol. |

Q.4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Q.5 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

Q.6 What is meant by hydroboration-oxidation reaction?
Illustrate it with an example.

Q.7 Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O .

Q.8 While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Q.9 Give the equations of reactions for the preparation of phenol from cumene.

Q.10 Write chemical reaction for the preparation of phenol from chlorobenzene.

Q.11 Write the mechanism of hydration of ethene to yield ethanol.

Q.12 You are given benzene, conc. H_2SO_4 and NaOH . Write the equations for the preparation of phenol using these reagents.

Q.13 Show how will you synthesise:

- (i) 1-phenylethanol from a suitable alkene.
- (ii) cyclohexylmethanol using an alkyl halide by an $\text{SN}2$ reaction.
- (iii) pentan-1-ol using a suitable alkyl halide?

Q.14 Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

Q.15 Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol ?

Q.16 Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

Q.17 Give equations of the following reactions:

- (i) Oxidation of propan-1-ol with alkaline KMnO₄ solution.
- (ii) Bromine in CS₂ with phenol.
- (iii) Dilute HNO₃ with phenol.
- (iv) Treating phenol with chloroform in presence of aqueous NaOH.

Q.18 Explain the following with an example.

- (i) Kolbe's reaction.
- (ii) Reimer-Tiemann reaction.
- (iii) Williamson ether synthesis.
- (iv) Unsymmetrical ether.

Q.19 Write the mechanism of acid dehydration of ethanol to yield ethene.

Q.20 How are the following conversions carried out?

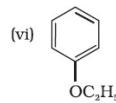
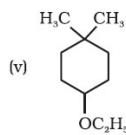
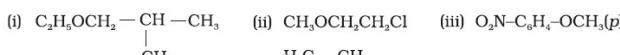
- (i) Propene → Propan-2-ol.
- (ii) Benzyl chloride → Benzyl alcohol.
- (iii) Ethyl magnesium chloride → Propan-1-ol.
- (iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.

Q.21 Name the reagents used in the following reactions:

- (i) Oxidation of a primary alcohol to carboxylic acid.
- (ii) Oxidation of a primary alcohol to aldehyde.
- (iii) Bromination of phenol to 2,4,6-tribromophenol.
- (iv) Benzyl alcohol to benzoic acid.
- (v) Dehydration of propan-2-ol to propene.
- (vi) Butan-2-one to butan-2-ol.

Q.22 Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Q .23 Give IUPAC names of the following ethers:



Q.24 Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

- (i) 1-Propoxypropane (ii) Ethoxybenzene (iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane

Q.25 Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

Q.26 How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

Q.27 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

Q.28 Write the equation of the reaction of hydrogen iodide with:

- (i) 1-propoxypropane (ii) methoxybenzene and (iii) benzyl ethyl ether.

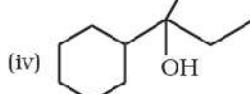
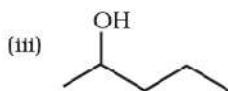
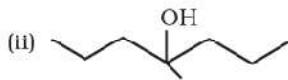
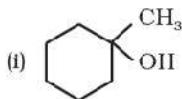
Q.29 Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

Q.30 Write the mechanism of the reaction of HI with methoxymethane.

Q.31 Write equations of the following reactions:

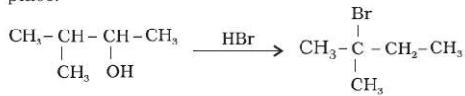
- (i) Friedel-Crafts reaction – alkylation of anisole.
- (ii) Nitration of anisole.
- (iii) Bromination of anisole in ethanoic acid medium.
- (iv) Friedel-Craft's acetylation of anisole.

Q.32 Show how would you synthesise the following alcohols from appropriate alkenes?



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Q .33 When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

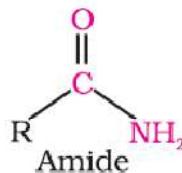
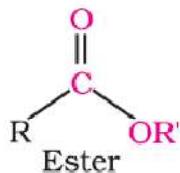
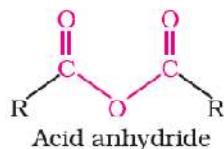
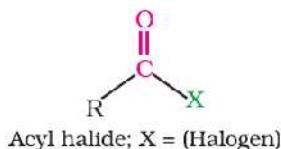
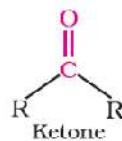
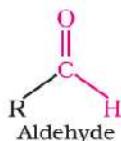


Give a mechanism for this reaction.

[Hint : The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.]

Acyl Groups

In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms. The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively.



Nomenclature and Structure of Carbonyl Group

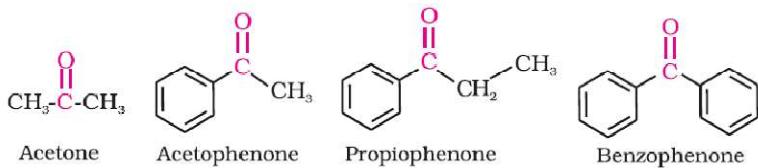
Aldehydes and ketones are the simplest and most important carbonyl compounds.

(a) *Common names*

Aldehydes and ketones are often called by their common names instead of IUPAC names. The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending *-ic* of acid with aldehyde.



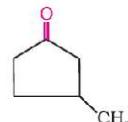
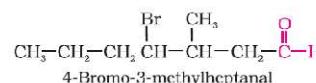
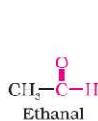
The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group.



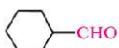
(b) IUPAC names

The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *-e* with *-al* and *-one* respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group.

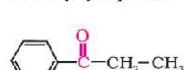
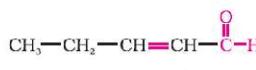
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3-Methylcyclopentanone



Cyclohexanecarbaldehyde



1-Phenylpropan-1-one

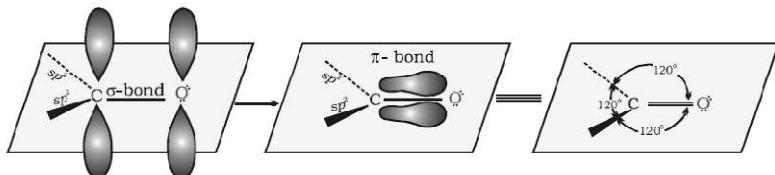
Table : Common and IUPAC Names of Some Aldehydes and Ketones

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
(CH ₃) ₂ CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexane	3-Methylcyclohexanecarbaldehyde
CH ₃ CH(OCH ₃)CHO	α-Methoxypropionaldehyde	2-Methoxypropanal
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Valeraldehyde	Pentanal
CH ₂ =CHCHO	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
CH ₃ COCH ₂ CH ₂ CH ₃	Methyl n-propyl ketone	Pentan-2-one
(CH ₃) ₂ CHCOCH(CH ₃) ₂	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
(CH ₃) ₂ C=CHCOCH ₃	Mesityl oxide	4-Methylpent-3-en-2-one

Structure of the Carbonyl Group

The carbonyl carbon atom is *sp*²-hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon

remains in its *p*-orbital and forms a π -bond with oxygen by overlap with *p*-orbital of an oxygen.



Q. Write the structures of the following compounds.

- | | |
|--|---------------------------|
| (i) α -Methoxypropionaldehyde | (ii) 3-Hydroxybutanal |
| (iii) 2-Hydroxycyclopentane carbaldehyde | (iv) 4-Oxopentanal |
| (v) Di-sec. butyl ketone | (vi) 4-Fluoroacetophenone |

Preparation of Aldehydes and Ketones

1. By oxidation of alcohols

2. By dehydrogenation of alcohols

3. From hydrocarbons

(i) *By ozonolysis of alkenes:* As we know, ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene.

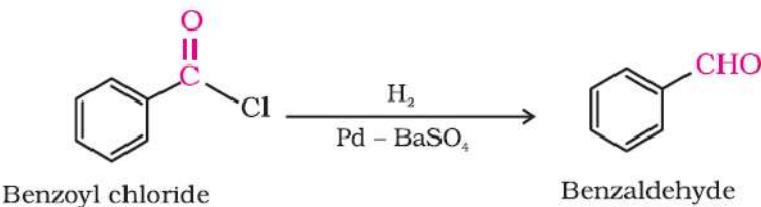
(ii) *By hydration of alkynes:* Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in this reaction .

Preparation of Aldehydes

1. From acyl chloride (acid chloride)

Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called

Rosenmund reduction.



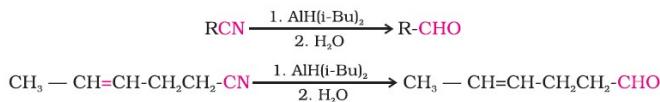
2. From nitriles and esters

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

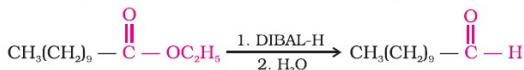


This reaction is called **Stephen** reaction.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:



Similarly, esters are also reduced to aldehydes with DIBAL-H.



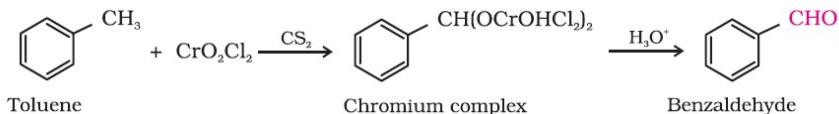
3. From hydrocarbons

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

(i) By oxidation of methylbenzene

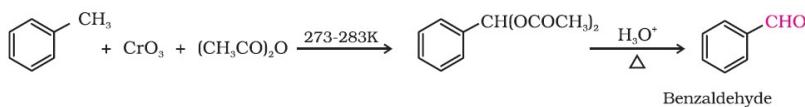
Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further.

(a) Use of chromyl chloride (CrO_2Cl_2): Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



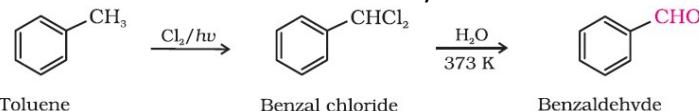
This reaction is called **Etard reaction**.

(b) Use of chromic oxide (CrO_3): Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



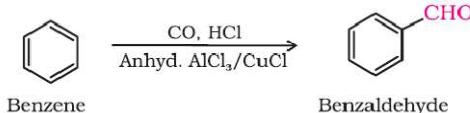
(ii) By side chain chlorination followed by hydrolysis

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.



(iii) By Gatterman-Koch reaction:

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.

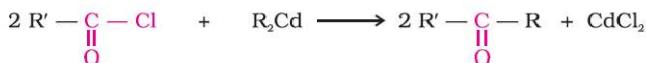
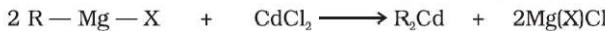


This reaction is known as **Gatterman-Koch** reaction.

Preparation of Ketones

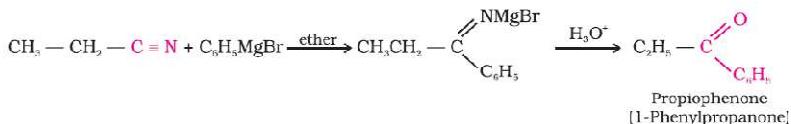
1. From acyl chlorides

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.



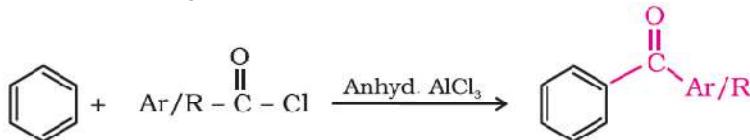
2. From nitriles

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



3. From benzene or substituted benzenes

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as Friedel-Crafts acylation reaction.



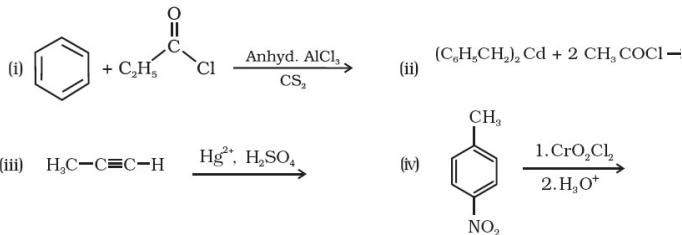
Q.

Give names of the reagents to bring about the following transformations:

- | | |
|---|------------------------------------|
| (i) Hexan-1-ol to hexanal | (ii) Cyclohexanol to cyclohexanone |
| (iii) <i>p</i> -Fluorotoluene to <i>p</i> -fluorobenzaldehyde | (iv) Ethanenitrile to ethanal |
| (v) Allyl alcohol to propenal | (vi) But-2-ene to ethanal |

Q.

Write the structures of products of the following reactions:



Physical Properties

Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant.

Arrange the following compounds in the increasing order of their boiling points:



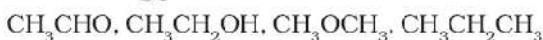
The molecular masses of these compounds are in the range of 72 to 74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. *n*-Pentane molecules have only weak **van der Waals forces**. Hence increasing order of boiling points of the given compounds is as follows:



Example

Solution

- Q. Arrange the following compounds in increasing order of their boiling points.

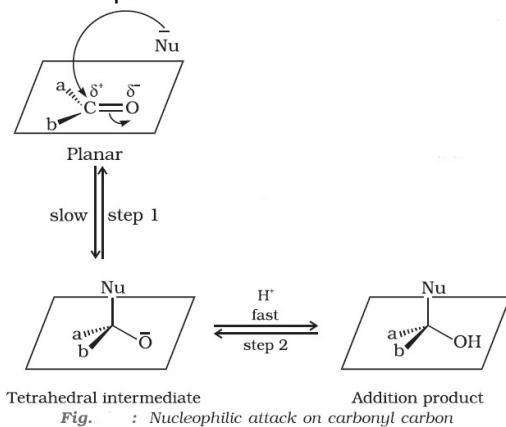


Chemical Reactions

1. Nucleophilic addition reactions

(i) Mechanism of nucleophilic addition reactions

A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced.



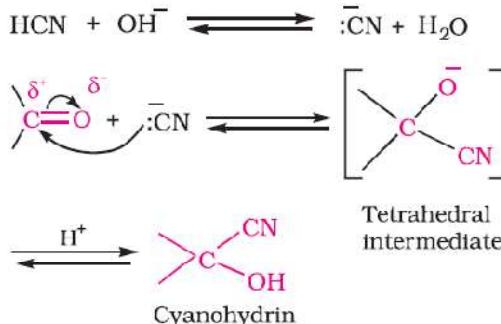
(ii) Reactivity

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in former.

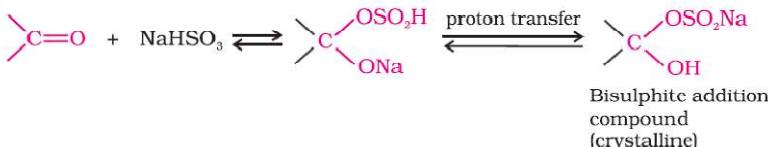
Q. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

(iii) Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:

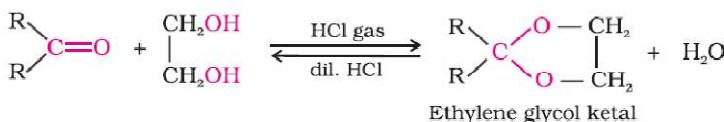
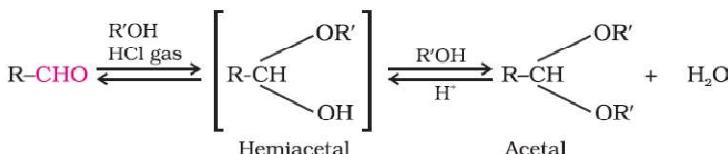
(a) Addition of hydrogen cyanide (HCN):



(b) Addition of sodium hydrogensulphite:



(d) Addition of alcohols:



(e) *Addition of ammonia and its derivatives:*

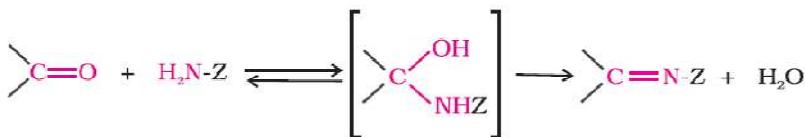


Table : Some N-Substituted Derivatives of Aldehydes and Ketones ($>\text{C}=\text{N}-\text{Z}$)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\text{>} \text{C}=\text{NH}$	Imine
-R	Amine	$\text{>} \text{C}=\text{NR}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$\text{>} \text{C}=\text{N-OH}$	Oxime
-NH ₂	Hydrazine	$\text{>} \text{C}=\text{N-NH}_2$	Hydrazone
	Phenylhydrazine	$\text{>} \text{C}=\text{N-NH-C}_6\text{H}_5$	Phenylhydrazone
	2,4-Dinitrophenylhydrazine	$\text{>} \text{C}=\text{N-NH-C}_6\text{H}_3(\text{NO}_2)_2\text{NO}_2$	2,4 Dinitrophenylhydrazone
	Semicarbazide	$\text{>} \text{C}=\text{N-NH-C}(=\text{O})-\text{NH}_2$	Semicarbazone

2. Reduction

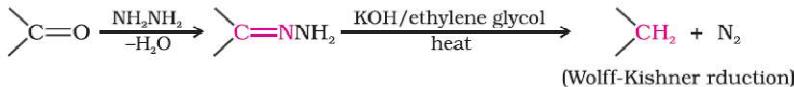
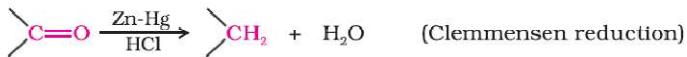
(i) *Reduction to alcohols:*

Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH₄) or lithium aluminium hydride (LiAlH₄) as well as by catalytic hydrogenation.

(ii) *Reduction to hydrocarbons:*

The carbonyl group of aldehydes and ketones is reduced to CH₂ group on treatment with zinc amalgam and concentrated hydrochloric acid [**Clemmensen reduction**] or with hydrazine followed by heating with sodium or

potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).

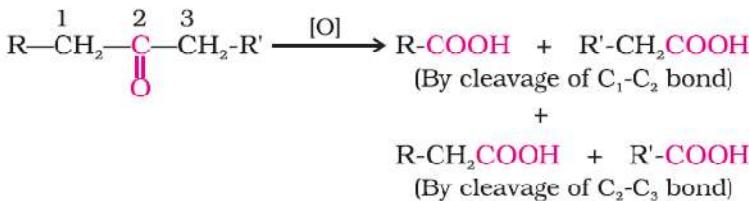


3. Oxidation

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.



Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



The mild oxidising agents given below are used to distinguish aldehydes from ketones:

(i) *Tollens' test:*

On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion.

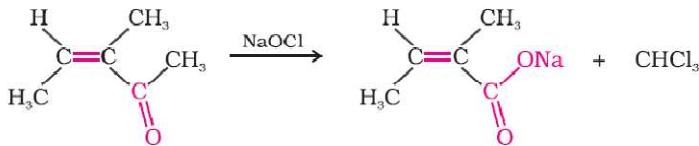


(ii) Fehling's test:

On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



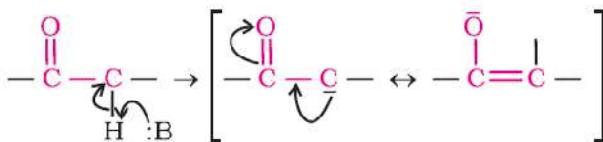
(iii) Oxidation of methyl ketones by haloform reaction:



Q. An organic compound (A) with molecular formula C₈H₈O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula C₇H₆O₂. Identify the compounds (A) and (B) and explain the reactions involved.

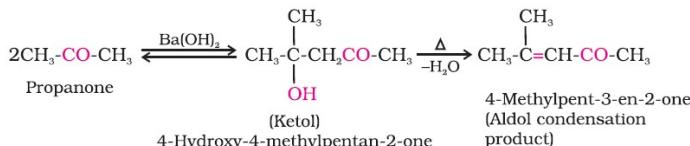
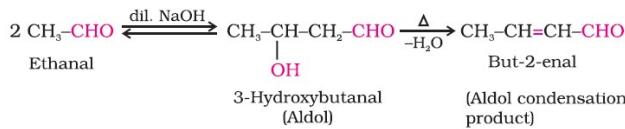
4. Reactions due to α -hydrogen

The acidity of α -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



(i) *Aldol condensation:* Aldehydes and ketones having at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -

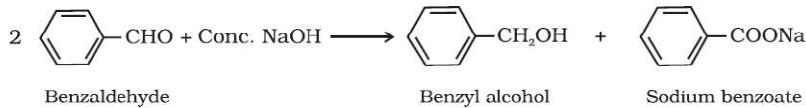
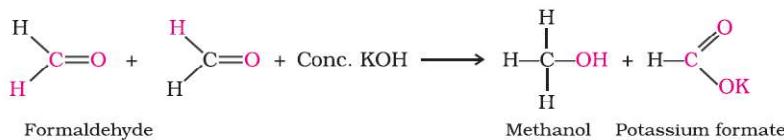
hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**.



5. Other reactions

(i) Cannizzaro reaction:

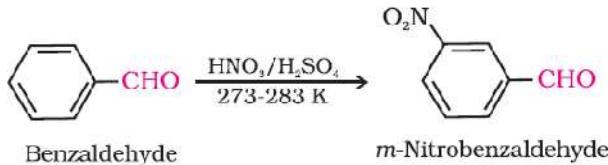
Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



(ii) Electrophilic substitution reaction:

Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a leaving group.

deactivating and *meta*-directing group.

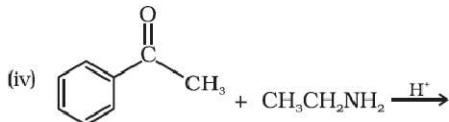
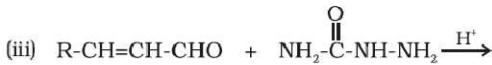
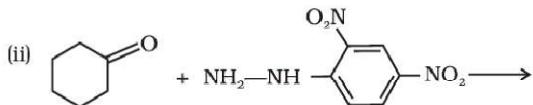
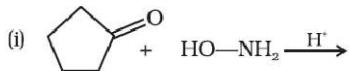


Q. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

- (i) Ethanal, Propanal, Propanone, Butanone.
- (ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

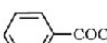
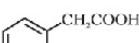
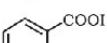
Hint: Consider steric effect and electronic effect.

Q. Predict the products of the following reactions:



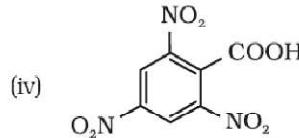
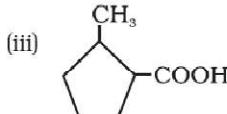
Nomenclature and Structure of Carboxyl Group

Table I Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH ₃ COOH	Acetic acid	Ethanone acid
CH ₃ CH ₂ COOH	Propanoic acid	Propanoic acid
CH ₃ CH ₂ CH ₂ COOH	Butyric acid	Butanoic acid
(CH ₃) ₂ CHCOOH	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC-CH ₂ -COOH	Malonic acid	Propanedioic acid
HOOC-(CH ₂) ₂ -COOH	Succinic acid	Butanedioic acid
HOOC-(CH ₂) ₃ -COOH	Glutaric acid	Pentanedioic acid
HOOC-(CH ₂) ₄ -COOH	Adipic acid	Hexanedioic acid
HOOC-CH ₂ -CH(COOH)-CH ₂ -COOH	-	Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzene carboxylic acid (Benzene acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

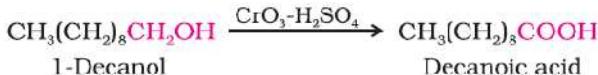
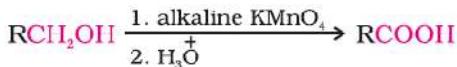
Q.

Give the IUPAC names of the following compounds:



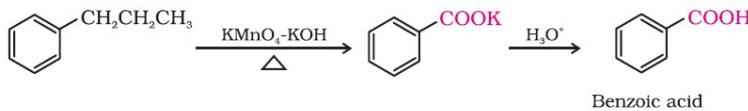
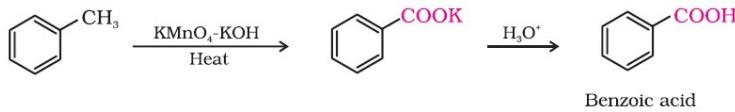
Methods of Preparation of Carboxylic Acids

1. From primary alcohols and aldehydes



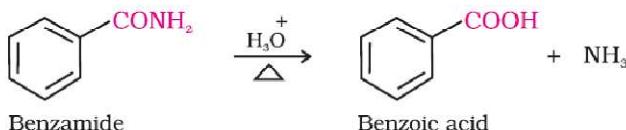
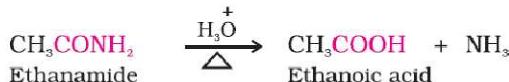
2. From alkylbenzenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents.

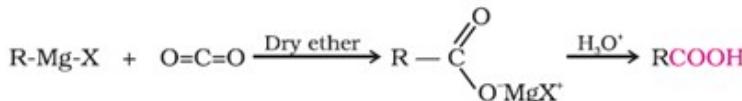


3. From nitriles and amides

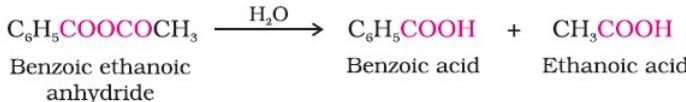
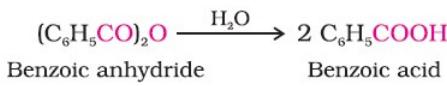
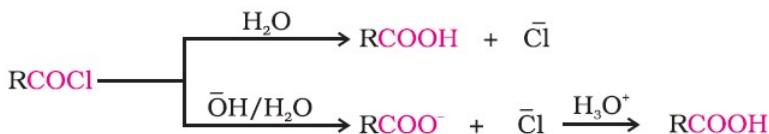
Nitriles are hydrolysed to amides and then to acids in the presence of H⁺ or OH⁻ as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.



4. From Grignard reagents

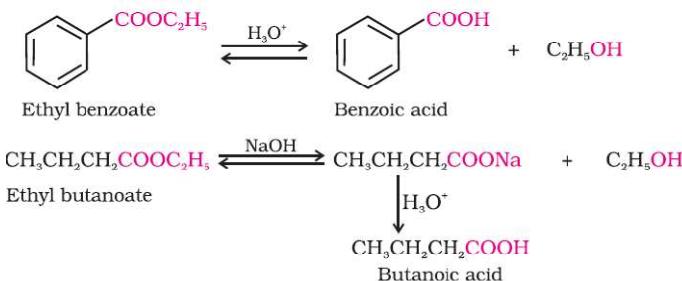


5. From acyl halides and anhydrides



6. From esters

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.



Q.

Write chemical reactions to affect the following transformations:

- (i) Butan-1-ol to butanoic acid
- (ii) Benzyl alcohol to phenylethanoic acid
- (iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid
- (iv) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid
- (v) Cyclohexene to hexane-1,6-dioic acid
- (vi) Butanal to butanoic acid.

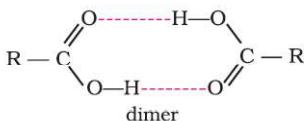
- Q. Show how each of the following compounds can be converted to benzoic acid.
- (i) Ethylbenzene (ii) Acetophenone
 - (iii) Bromobenzene (iv) Phenylethene (Styrene)

Physical Properties

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of

hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.



*In vapour state or in
aprotic solvent*

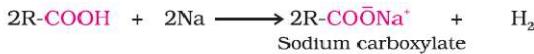


Chemical Reactions

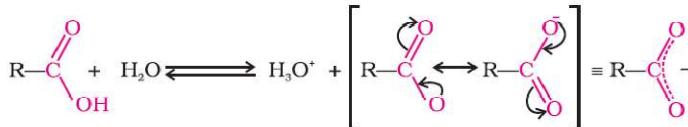
Reactions Involving Cleavage of O–H Bond

Acidity

Reactions with metals and alkalies



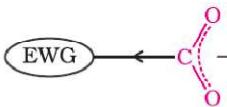
Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



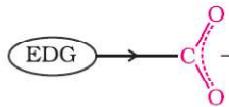
Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols (pK_a is ~ 16 for ethanol and 10 for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds.

Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



Electron withdrawing group (EWG)
stabilises the carboxylate anion
and strengthens the acid

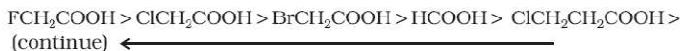


Electron donating group (EDG)
destabilises the carboxylate
anion and weakens the acid

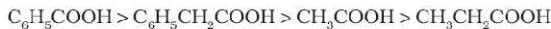
The effect of the following groups in increasing acidity order is



Thus, the following acids are arranged in order of decreasing acidity
(based on pK_a values):



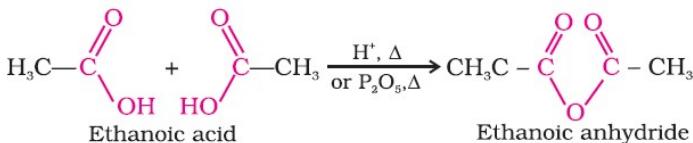
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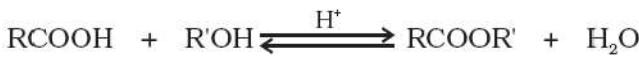
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Reactions Involving Cleavage of C–OH Bond

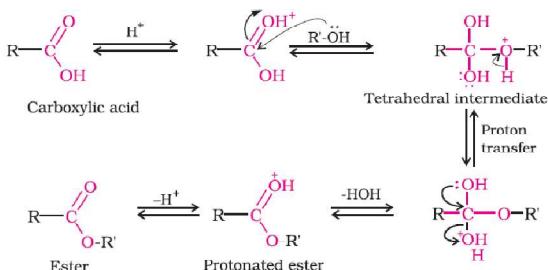
1. Formation of anhydride



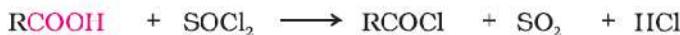
2. Esterification



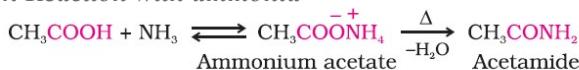
Mechanism of esterification of carboxylic acids: The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-\text{OH}_2^+$ group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



3. Reactions with PCl_5 , PCl_3 and $SOCl_2$

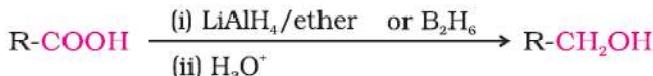


4. Reaction with ammonia



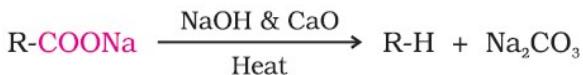
Reactions Involving –COOH Group

1. Reduction



2. Decarboxylation

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

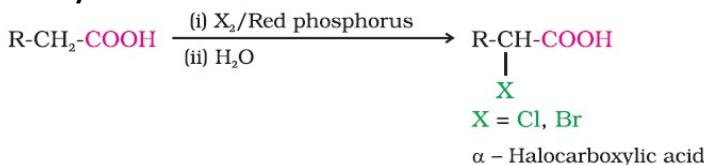


Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis**.

Substitution Reactions in the Hydrocarbon Part

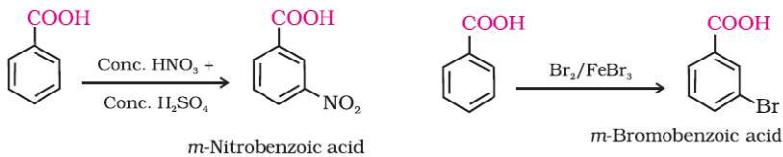
1. Halogenation

Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



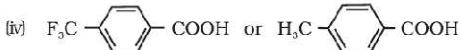
2. Ring substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo **Friedel-Crafts reaction** (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).



Q. Which acid of each pair shown here would you expect to be stronger?

- (i) $\text{CH}_3\text{CO}_2\text{H}$ or $\text{CH}_2\text{FCO}_2\text{H}$ (ii) $\text{CH}_2\text{FCO}_2\text{H}$ or $\text{CH}_2\text{ClCO}_2\text{H}$
(iii) $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$ or $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$



NCERT Exercises

Q2. Name the following compounds according to IUPAC system of nomenclature:

- | | |
|--|---|
| (i) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CHO}$ | (ii) $\text{CH}_3\text{CH}_2\text{COCH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{Cl}$ |
| (iii) $\text{CH}_3\text{CH}=\text{CHCHO}$ | (iv) $\text{CH}_3\text{COCH}_2\text{COCH}_3$ |
| (v) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{COCH}_3$ | (vi) $(\text{CH}_3)_3\text{CCH}_2\text{COOH}$ |
| (vii) $\text{OHCC}_6\text{H}_4\text{CHO}-p$ | |

Q3.

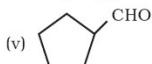
Draw the structures of the following compounds.

- | | |
|--|-------------------------------------|
| (i) 3-Methylbutanal | (ii) <i>p</i> -Nitropropiophenone |
| (iii) <i>p</i> -Methylbenzaldehyde | (iv) 4-Methylpent-3-en-2-one |
| (v) 4-Chloropentan-2-one | (vi) 3-Bromo-4-phenylpentanoic acid |
| (vii) <i>p,p'</i> -Dihydroxybenzophenone | (viii) Hex-2-en-4-ynoic acid |

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Q4. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

- (i) $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$ (ii) $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}(\text{CH}_3)\text{CHO}$
 (iii) $\text{CH}_3(\text{CH}_2)_5\text{CHO}$ (iv) $\text{Ph}-\text{CH}=\text{CH}-\text{CHO}$



- (vi) PhCOPh

Q5.

Draw structures of the following derivatives.

- (i) The 2,4-dinitrophenylhydrazone of benzaldehyde
 - (ii) Cyclopropanone oxime
 - (iii) Acetaldehydedimethylacetal
 - (iv) The semicarbazone of cyclobutanone
 - (v) The ethylene ketal of hexan-3-one
 - (vi) The methyl hemiacetal of formaldehyde

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Q6. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

- | | |
|---|------------------------------|
| (i) PhMgBr and then H_3O^+ | (ii) Tollens' reagent |
| (iii) Semicarbazide and weak acid | (iv) Excess ethanol and acid |
| (v) Zinc amalgam and dilute hydrochloric acid | |

Q7. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

- | | | |
|--------------------------|-----------------------|--------------------------|
| (i) Methanal | (ii) 2-Methylpentanal | (iii) Benzaldehyde |
| (iv) Benzophenone | (v) Cyclohexanone | (vi) 1-Phenylpropanone |
| (vii) Phenylacetaldehyde | (viii) Butan-1-ol | (ix) 2,2-Dimethylbutanal |

- Q8.** How will you convert ethanal into the following compounds?
(i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid

- Q9.** Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

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- Q10.** An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

- Q11.** An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Q12.

Arrange the following compounds in increasing order of their property as indicated:

- (i) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)
- (ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$,
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (acid strength)
- (iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid,
4-Methoxybenzoic acid (acid strength)

Q13. Give simple chemical tests to distinguish between the following pairs of compounds.

- (i) Propanal and Propanone (ii) Acetophenone and Benzophenone
- (iii) Phenol and Benzoic acid (iv) Benzoic acid and Ethyl benzoate
- (v) Pentan-2-one and Pentan-3-one (vi) Benzaldehyde and Acetophenone
- (vii) Ethanal and Propanal

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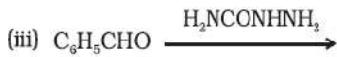
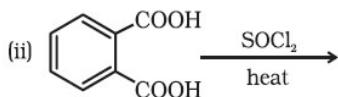
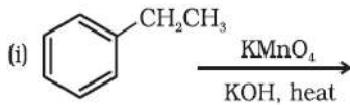
Q14. How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom

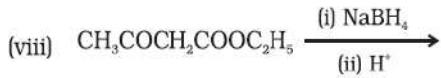
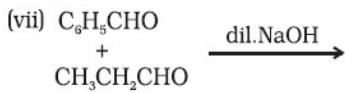
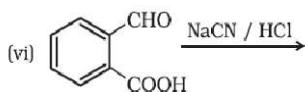
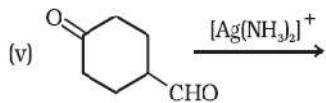
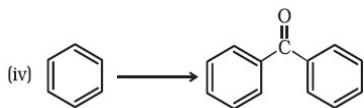
- (i) Methyl benzoate
- (ii) *m*-Nitrobenzoic acid
- (iii) *p*-Nitrobenzoic acid
- (iv) Phenylacetic acid
- (v) *p*-Nitrobenzaldehyde.

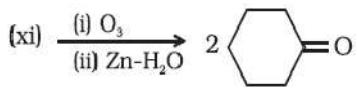
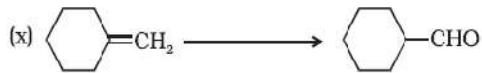
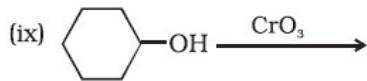
Q15. How will you bring about the following conversions in not more than two steps?

- (i) Propanone to Propene
- (ii) Benzoic acid to Benzaldehyde
- (iii) Ethanol to 3-Hydroxybutanal
- (iv) Benzene to *m*-Nitroacetophenone
- (v) Benzaldehyde to Benzophenone
- (vi) Bromobenzene to 1-Phenylethanol
- (vii) Benzaldehyde to 3-Phenylpropan-1-ol
- viii) Benzaldehyde to α -Hydroxyphenylacetate acid
- (ix) Benzoic acid to *m*- Nitrobenzyl alcohol

Q17. Complete each synthesis by giving missing starting material, reagent or products







- Q18.** Give plausible explanation for each of the following:
- (i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
 - (ii) There are two -NH₂ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
 - (iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.
- Q19.** An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

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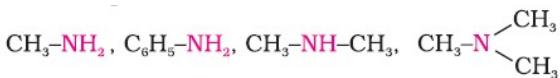
Q20. *Ways* **are** *more* *numerous* *than* *estimates* *from* *surveys*.

Amines

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s).

AMINES

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups. For example:



Structure of Amines

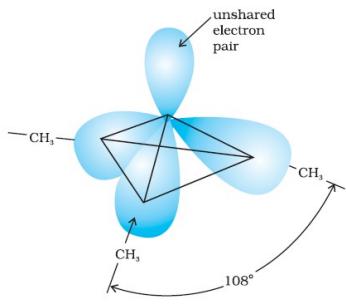
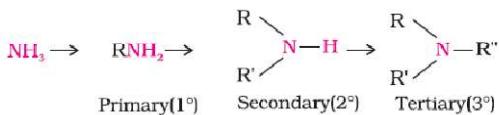


Fig. Pyramidal shape of trimethylamine

Classification



Test Series

Test (Some Basic concepts of chemistry)

Time Allowed : 1 hour

Maximum Marks :

29

Please read the instructions carefully. You will be allotted 5 minutes specifically for this purpose.

Instructions

A. General

1. Blank papers, clipboards, log tables, slide rules, calculators, cellular phones, pagers, and electronic gadgets in any form are not allowed.
2. Do not break the seals of the question-paper booklet before instructed to do so by the invigilators.

B. Question paper format and Marking Scheme :

1. This question paper consists of 12 questions carrying a total of 26 Marks, Questions 1 to 3 carry 1 mark each, Questions 4 to 8 carry 2 marks each , Questions 9 to 10 carry 3 marks each and questions 11 to 12 carry five marks each.

Q1 : Calculate molecular mass of glucose ($C_6H_{12}O_6$) molecule. 1 Marks

Q2 : Classify following as pure substances and mixtures –
Air, glucose, gold, sodium and milk.

1 Marks

Q3 : State Avogadro's law.

1 Marks

Q4 : A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

2 Marks

Q5 : Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

2 Marks

Q6 : Calculate the amount of water (g) produced by the combustion of 16 g of methane.

2 Marks

Q7 : Write the seven fundamental quantities & their units.

2 Marks

Q8 : What is the difference between mass & weight? How is mass measured in laboratory?

2 Marks

Q9: A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas ?

3 Marks

Q10 : How many moles of methane are required to produce 22 g $\text{CO}_2(\text{g})$ after combustion?

3 Marks

Q11 : 50.0 kg of $\text{N}_2(\text{g})$ and 10.0 kg of $\text{H}_2(\text{g})$ are mixed to produce $\text{NH}_3(\text{g})$. Calculate the $\text{NH}_3(\text{g})$ formed. Identify the limiting reagent in the production of NH_3 in this situation. 5 Marks

Q12 : The density of 3 M solution of NaCl is 1.25 g mL^{-1} . Calculate molality of the solution.

5 Marks

Test (Structure of Atom)

Time Allowed : 1 hour

Maximum Marks :

31

Please read the instructions carefully. You will be allotted 5 minutes specifically for this purpose.

Instructions

A. General

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2. Do not break the seals of the question-paper booklet before instructed to do so by the invigilators.

B. Question paper format and Marking Scheme :

1. This question paper consists of 9 questions carrying a total of 31 Marks, Questions 1 to 3 carry 1 mark each, Questions 4 to 6 carry 2 marks each , Questions 7 to 10 carry 3 marks each and questions 11 to 12 carry five marks each.

Q1 : Define photoelectric effect.

1 Marks

Q2 : Define black body radiation.

1 Marks

Q3 : Give the range of wavelength of the visible spectrum.
1 Marks

Q4 : Calculate the wavelength corresponding to a frequency of 98.8MHz.
2 Marks

Q5 : What is the e/m ratio of an electron?
2 Marks

Q6 : Why Rutherford's model could not explain the stability of an atom?
2 Marks

Q7 : Which experiment led to the discovery of electrons and how?
3 Marks

Q8 : Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol⁻¹
3 Marks

Q9 : What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy?

3 Marks

Q10 : A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57μm. Calculate the rate of emission of quanta per second.
3 Marks

Q11 : What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n = 4 to n = 2 of He⁺ spectrum?
5 Marks

Q12 : An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons, find the symbol of the ion.

5 Marks

Test (Classification of Elements and Periodicity in Properties)

Time Allowed : 1 hour

Maximum Marks :

20

Please read the instructions carefully. You will be allotted 5 minutes specifically for this purpose.

Instructions

A. General

1. Blank papers, clipboards, log tables, slide rules, calculators, cellular phones, pagers, and electronic gadgets in any form are not allowed.
2. Do not break the seals of the question-paper booklet before instructed to do so by the invigilators.

B. Question paper format and Marking Scheme :

1. This question paper consists of 9 questions carrying a total of 31 Marks, Questions 1 to 2 carry 1 mark each, Questions 3 to 4 carry 2 marks each , Questions 5 to 7 carry 3 marks each and question 8 carries five marks.

Q1 : How does atomic size change in a group?

1 Marks

Q2 : What is the basic theme of organisation in the periodic table?

1 Marks

Q3 : Consider the following species : N³⁻, O²⁻, F⁻, Na⁺, Mg²⁺ and Al³⁺

- (a) What is common in them?
(b) Arrange them in the order of increasing ionic radii.
2 Marks

Q4 : (a) What is an amphoteric oxide?

- (b) Define a neutral oxide.
2 Marks

Q5 : (a) Why do Na and K have similar properties?

- (b) Why does lithium form covalent bond unlike other alkali which forms ionic bond?
3 Marks

Q6 : Na⁺ has higher value of ionization enthalpy than Ne, though both have same electronic configuration.

3 Marks

Q7 : Among the second period elements the actual ionization enthalpies are in the order

Li < B < Be < C < O < N < F < Ne. Explain why

- (i) Be has higher $\Delta i H$ than B
(ii) O has lower $\Delta i H$ than N and F?

3 Marks

Q8: (i) Arrange the following elements in the increasing order of metallic character :

Si, Be, Mg, Na, P

(ii) Among the elements

B, Al, C and Si

- (a) Which has the highest first ionization enthalpy?
- (b) Which has the largest atomic radius?

5 Marks