

# केन्द्रीय विद्यालय संगठन KENDRIYA VIDYALAYA SANGATHAN

शिक्षा एवं प्रशिक्षण का आंचलिक संस्थान, चंडीगढ़

ZONAL INSTITUTE OF EDUCATION AND TRAINING, CHANDIGARH



STUDY MATERIAL

SESSION– 2021-22

CLASS – XII

CHEMISTRY

TERM - II

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## DIRECTOR'S MESSAGE



Our aim is to provide such brief study materials and sample papers to the student that not only guides students to the path of success, but also inspires them to recognize and explore their own inner potential. The Board exam preparation is based on three pillars – **Concept Clarity, Contextual familiarity and Application Expertise**. Our innovative and dedicated teaching materials ensure that every student gets a firm grip of each of these pillars so very essential for these arduous preparations.

We also understand the importance of CBSE board exam as students' future goal depends upon the performance in board exams. We know that in pandemic situation the students feel a lot of pressure of performance in board exam. It is very important to develop the right exam temperament in students so they can tackle the pressure & surprises easily. In this direction, to release such brief study materials and sample papers will help to the students a lot.



**CLASS XII TERM-II SESSION 2021-22**  
**SUBJECT: CHEMISTRY (043)**

S.No.	UNIT	No. of Periods	MARKS
1	Electrochemistry	7	13
2	Chemical Kinetics	5	
3	Surface Chemistry	5	
4	d-and f-Block Elements	7	9
5	Coordination Compounds	8	
6	Aldehydes, Ketones and Carboxylic Acids	10	13
7	Amines	7	
	TOTAL	49	35

**SYLLABUS FOR TERM-II CHEMISTRY (043) SESSION 2021-22**

**Electrochemistry:** Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, Conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis.

**Chemical Kinetics:** Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions).

**Surface Chemistry:** Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, colloidal state: distinction between true solutions, colloids and suspension; lyophilic, lyophobic, multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation.

**d-and f-Block Elements:** General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation.

Lanthanoids - Electronic configuration, oxidation states and lanthanide contraction and its consequences.

**Coordination Compounds:** Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT.

**Aldehydes, Ketones and Carboxylic Acids: Aldehydes and Ketones:** Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of Nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.

Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

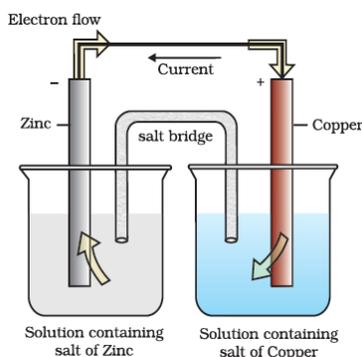
**Amines:** Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

### UNIT 3 ELECTROCHEMISTRY

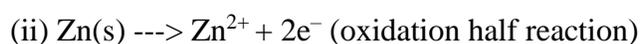
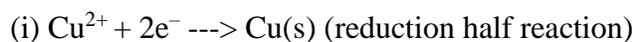
**Electrochemistry** is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadget like heater, fan, geyser, etc.

Daniell cell: Daniell cell is the one such cell in which the following redox reaction occurs.



**Fig. 3.1:** Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.



The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half-cell reaction and the zinc electrode, the oxidation half-cell reaction.

#### **Electrode potential/Standard electrode potential:**

A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called

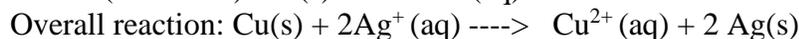
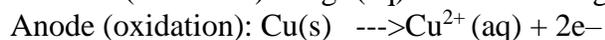
**cathode** and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (e.m.f) of the cell when no current is drawn through the cell.

**EMF of a cell:** The e.m.f of the cell is positive and is given by the potential of the half-cell on the right-hand side minus the potential of the half-cell on the left-hand side i.e.,

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

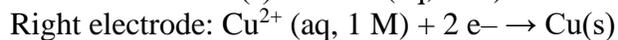
This is illustrated by the following example: Half-cell reactions:



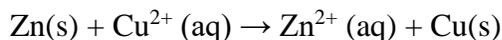
Silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as:  $\text{Cu}(\text{s})|\text{Cu}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag}(\text{s})$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}^+/\text{Ag}} - E_{\text{Cu}^{2+}/\text{Cu}}$$

In view of this convention, the half reaction for the Daniell cell in Fig. 3.1 can be written as:



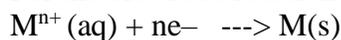
The overall reaction of the cell is the sum of above two reactions and we obtain the equation:



$$\begin{aligned} \text{e.m.f of the cell} &= E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}} \\ &= 0.34\text{V} - (-0.76)\text{V} = 1.10\text{V} \end{aligned}$$

### Nernst equation and its application to chemical cells:

For the electrode reaction:



The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(\text{M}^{n+}/\text{M})} = E^{\ominus}_{(\text{M}^{n+}/\text{M})} - \frac{RT}{nF} \ln \frac{[\text{M}]}{[\text{M}^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(\text{M}^{n+}/\text{M})} = E^{\ominus}_{(\text{M}^{n+}/\text{M})} - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

R is gas constant ( $8.314\text{ JK}^{-1}\text{ mol}^{-1}$ ), F is Faraday constant ( $96487\text{ C mol}^{-1}$ ), T is temperature in kelvin and  $[\text{M}^{n+}]$  is the concentration of the species,  $\text{M}^{n+}$ .

In Daniell cell, the electrode potential for any given concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions,

For Cathode:

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E_{(\text{Cu}^{2+}/\text{Cu})}^{\ominus} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]}$$

For Anode:

$$E_{(\text{Zn}^{2+}/\text{Zn})} = E_{(\text{Zn}^{2+}/\text{Zn})}^{\ominus} - \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]}$$

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

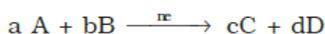
$$E_{\text{cell}} = E_{\text{cell}}^0 - (RT/2F) \ln \{[\text{Zn}^{2+}] / [\text{Cu}^{2+}]\}$$

$E_{\text{cell}}$  depends on the concentration of both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions. It increases with increase in the concentration of  $\text{Cu}^{2+}$  ions and decrease in the concentration of  $\text{Zn}^{2+}$  ions.

We know that,  $\ln X = 2.303 \log X$ ,  $R$  is gas constant ( $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ),  $F$  is Faraday constant ( $96487 \text{ C mol}^{-1}$ ),  $T$  is temperature in kelvin,  $298\text{K}$ . Then

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.059/2) \log \{[\text{Zn}^{2+}] / [\text{Cu}^{2+}]\}$$

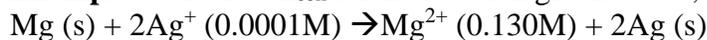
For a general electrochemical reaction of the type:



Nernst equation can be written as:

$$\begin{aligned} E_{(\text{cell})} &= E_{(\text{cell})}^{\ominus} - \frac{RT}{nF} \ln Q \\ &= E_{(\text{cell})}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \end{aligned}$$

**Example:** Calculate  $E_{\text{cell}}$  for the reaction given below, if  $E_{\text{cell}}^0 = 3.17\text{V}$



**Solution:**

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.059/2) \log \{[\text{Mg}^{2+}] / [\text{Ag}^+]^2\}$$

$$= 3.17 - 0.0295 \log [(0.130)/(0.0001)^2]$$

$$= 3.17 \text{ V} - 0.21 \text{ V} = 2.96 \text{ V}$$

#### Equilibrium Constant from Nernst Equation:

If the circuit in Daniell cell (Fig. 3.1) is closed then we note that the reaction  $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$  takes place and as time passes, the concentration of  $\text{Zn}^{2+}$  keeps on increasing while the concentration of  $\text{Cu}^{2+}$  keeps on decreasing.

At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E_{\text{cell}} = 0 = E_{\text{cell}}^0 - (RT/2F) \ln \{[\text{Zn}^{2+}] / [\text{Cu}^{2+}]\}$$

$$E_{\text{cell}}^0 = (RT/2F) \ln \{[\text{Zn}^{2+}] / [\text{Cu}^{2+}]\}$$

But at equilibrium,

$$[\text{Zn}^{2+}] / [\text{Cu}^{2+}] = K_c$$

at  $T = 298\text{K}$  the above equation can be written as

$$E_{\text{cell}}^0 = (0.059/2) \log K_c = 1.10 \text{ V} \quad (E_{\text{cell}}^0 = 1.10 \text{ V})$$

$$\log K_c = [(1.10\text{V} \times 2)]/0.059 = 37.288$$

$$K_c = 2 \times 10^{37} \text{ at } 298\text{K}.$$

In general,

$$E_{\text{cell}}^0 = (2.303RT/nF) \ln K_c$$

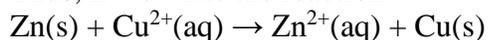
This gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place.

### Electrochemical Cell and Gibbs Energy of the Reaction:

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is  $E$  and  $nF$  is the amount of charge passed and  $\Delta_r G$  is the Gibbs energy of the reaction, then  $\Delta_r G = -nFE_{\text{cell}}$

$E_{\text{cell}}$  is an intensive parameter but  $\Delta_r G$  is an extensive thermodynamic property and the value depends on  $n$ .

Thus, if we write the reaction



$$\Delta_r G = -2 F E_{\text{cell}}$$

If the concentration of all the reacting species is unity, then  $E_{\text{cell}} = E_{\text{cell}}^0$

$$\Delta_r G^0 = -n F E_{\text{cell}}^0$$

We can calculate equilibrium constant by the equation:

$$\Delta_r G^0 = -RT \ln K.$$

**Example:** The standard electrode potential for Daniell cell is  $1.1\text{V}$ . Calculate the standard Gibbs energy for the reaction:  $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

$$\text{Solution: } \Delta_r G^0 = -n F E_{\text{cell}}^0$$

The value of  $n$  in the above equation is 2,  $F = 96500 \text{ C mol}^{-1}$  and  $E_{\text{cell}}^0 = 1.1 \text{ V}$

$$\text{Therefore, } \Delta_r G^0 = -2 \times 1.1\text{V} \times 96500 \text{ C mol}^{-1}$$

$$= -212300 \text{ J mol}^{-1}$$

$$= -212.3 \text{ kJ mol}^{-1}$$

### Conductance of Electrolytic Solutions:

The electrical resistance is represented by the symbol ' $R$ ' and it is measured in ohm ( $\Omega$ ). The electrical resistance of any object is directly proportional to its length,  $l$ , and inversely proportional to its area of cross section,  $A$ . That is,

$$R \propto l/A \text{ or } R = \rho (l/A)$$

The constant of proportionality,  $\rho$  (rho), is called **resistivity** (specific resistance). Its SI units are ohm metre ( $\Omega \text{ m}$ ) or ohm centimetre ( $\Omega \text{ cm}$ ).

The resistivity for a substance is its resistance when it is one metre long and its area of cross section is one  $\text{m}^2$ . It can be seen that:

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

The inverse of resistance,  $R$ , are called **conductance**,  $G$ , and we have the relation:

$$G = 1/R = A/\rho l = \kappa (A/l) \quad [\kappa = 1/\rho]$$

The SI unit of conductance is Siemens, represented by the symbol 'S' and is equal to  $\text{ohm}^{-1}$  (also known as mho) or  $\Omega^{-1}$ .

The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol,  $\kappa$  (Greek, kappa). The SI units of conductivity are  $\text{S m}^{-1}$ . Conductivity of a material in  $\text{S m}^{-1}$  is its conductance when it is 1 m long and its area of cross section is  $1 \text{ m}^2$ . It may be noted that  $1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}$ .

**Electrical conductance** through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on:

- (i) The nature and structure of the metal
- (ii) The number of valence electrons per atom
- (iii) Temperature (it decreases with increase of temperature).

When electrolytes are dissolved in water its conductivity increases. The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:

- (i) The nature of the electrolyte added
- (ii) Size of the ions produced and their solvation
- (iii) The nature of the solvent and its viscosity
- (iv) Concentration of the electrolyte
- (v) Temperature (it increases with the increase of temperature)

**Conductivity of Ionic Solutions:** In the conductivity cell the solution confined between the electrodes is a column of length  $l$  and area of cross section  $A$ . The resistance of such a column of solution is given by the equation:

$$R = \rho l/A = l/\kappa A$$

The quantity  $l/A$  is called cell constant denoted by the symbol,  $G^*$ . It depends on the distance between the electrodes and their area of cross-section.

The cell constant,  $G^*$ , is then given by the equation:

$$G^* = l/A = R \kappa$$

$$K = \text{cell constant}/R = G^*/R$$

**Molar conductivity:** It is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. It is denoted by the symbol  $\Lambda_m$  ( $\Lambda = \text{lambda}$ ). It is related to the conductivity of the solution by the equation:

$$\text{Molar conductivity} = \Lambda_m = \kappa/c$$

In the above equation, if  $\kappa$  is expressed in  $\text{S m}^{-1}$  and the concentration,  $c$  in  $\text{mol m}^{-3}$  then the units of  $\Lambda_m$  is in  $\text{S m}^2 \text{ mol}^{-1}$ .

$$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1}) = [\kappa (\text{S cm}^{-1}) \times 1000 (\text{cm}^3/\text{L})] / \text{Molarity (mol/L)}$$

$$\Lambda_m = [\kappa \times 1000] / \text{Molarity}$$

$$1 \text{ S m}^2 \text{ mol}^{-1} = 10^4 \text{ S cm}^2 \text{ mol}^{-1} \text{ or}$$

$$1 \text{ S cm}^2 \text{ mol}^{-1} = 10^{-4} \text{ S m}^2 \text{ mol}^{-1}.$$

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

Solution:

$$A = \pi r^2 = 3.14 \times 0.52 \text{ cm}^2 = 0.785 \text{ cm}^2 = 0.785 \times 10^{-4} \text{ m}^2$$

$$l = 50 \text{ cm} = 0.5 \text{ m}$$

$$R = \rho l / A$$

$$\rho \text{ (resistivity)} = RA/l = [5.55 \times 10^3 \text{ ohm} \times 0.785 \text{ cm}^2] / 50 \text{ cm} = 87.135 \text{ ohm cm}$$

$$\text{Conductivity } (\kappa) = 1/\rho = [1 / 87.135] \text{ S cm}^{-1} = 0.01148 \text{ S cm}^{-1}$$

$$\begin{aligned} \text{Molar conductivity, } \Lambda_m &= [\kappa \text{ (S cm}^{-1}) \times 1000 \text{ (cm}^3\text{/L)}] / \text{Molarity (mol/L)} \\ &= [0.01148 \times 1000] / 0.05 \\ &= 229.6 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

### Variation of Conductivity and Molar Conductivity with Concentration:

Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decrease on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.

This is clear from the equation:  $G = \kappa A/l$  (both  $A$  and  $l$  is unity in their units in m or cm)

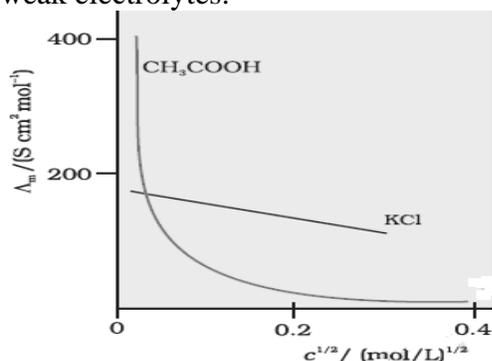
Molar conductivity of a solution at a given concentration is the conductance of the volume  $V$  of solution containing one mole of electrolyte kept between two electrodes with area of cross section  $A$  and distance of unit length. Therefore,

$$\Lambda_m = \kappa A/l$$

Since  $l = 1$  and  $A = V$  (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Molar conductivity increases with decrease in concentration. This is because the total volume,  $V$ , of solution containing one mole of electrolyte also increases. At a given concentration,  $\Lambda_m$  can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol  $\Lambda_m^0$ . The variation in  $\Lambda_m$  with concentration is different for strong and weak electrolytes.



**Fig. 3.6:** Molar conductivity  $\Lambda_m$  versus  $c^{1/2}$  for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

### Strong Electrolytes

For strong electrolytes,  $\Lambda_m$  increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \Lambda_m^0 - A c^{1/2}$$

If we plot  $\Lambda_m$  against  $c^{1/2}$ , we obtain a straight line with intercept equal  $\Lambda_m^0$  and slope equal to 'A'. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, CaCl<sub>2</sub>, MgSO<sub>4</sub> are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for 'A'.

**Kohlrausch's 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.

If  $\lambda_{\text{Na}^+}^{\circ}$  and  $\lambda_{\text{Cl}^-}^{\circ}$  are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda_m^0 = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}$$

In general, if an electrolyte on dissociation gives  $\nu_+$  cations and  $\nu_-$  anions then its limiting molar conductivity is given by:  $\Lambda_m^0 = \nu_+ \lambda_+^{\circ} + \nu_- \lambda_-^{\circ}$

$\lambda_+^{\circ} + \lambda_-^{\circ}$  are the limiting molar conductivities of the cation and anion respectively.

### Weak Electrolytes

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations, for such electrolytes, the change in  $\Lambda_m$  with dilution is due to increase in the degree of dissociation.

At any concentration  $c$ , if  $\alpha$  is the degree of dissociation, then

$$\alpha = \Lambda_m / \Lambda_m^0$$

**Example:**  $\Lambda_m^0$  for NaCl, HCl and CH<sub>3</sub>COONa are 126.4, 425.9 and 91.0 S cm<sup>2</sup> mol<sup>-1</sup> respectively. Calculate  $\Lambda_m^0$  for CH<sub>3</sub>COOH.

**Solution:**  $\Lambda_m^0$  (HCl) +  $\Lambda_m^0$  (CH<sub>3</sub>COONa) -  $\Lambda_m^0$  (NaCl)  
425.9 + 91.0 - 126.4 = 390.5 S cm<sup>2</sup> mol<sup>-1</sup>

**ELECTROLYSIS:** It is a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten (fused) state of electric current.

### Quantitative Aspects of Electrolysis

#### Faraday's Laws of Electrolysis:

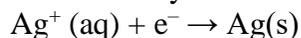
(i) **Faraday first law of electrolysis:** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

$w \propto Q$  or  $w = ZQ$ , Where Z is called electrochemical equivalent. If a current of I amperes is passed for t seconds, then  $Q = It$  so that,  $w = ZIt$

(ii) **Faraday first law of electrolysis:** 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 ÷ Number of electrons required to reduce the cation). For example, when same current is passed through two electrolytic solutions, containing copper sulphate and silver nitrate connected in series, the weight of copper and silver deposited are:

(Weight of Cu deposited) / (Weight of Cu deposited) = (Eq. wt. of Cu) / (Eq. wt. of Ag)

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:



One mole of the electron is required for the reduction of one mole of silver ions.

The charge on one electron is equal to  $1.6021 \times 10^{-19} \text{ C}$ .

Therefore, the charge on one mole of electrons is equal to:

$$N_A \times 1.6021 \times 10^{-19} \text{ C} = 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.6021 \times 10^{-19} \text{ C} = 96487 \text{ C mol}^{-1}$$

This quantity of electricity is called **Faraday** and is represented by the symbol **F**.

For approximate calculations we use  $1\text{F} \approx 96500 \text{ C mol}^{-1}$ .



For the above electrode reactions, one mole of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively.

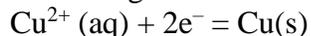
Example: A solution of  $\text{CuSO}_4$  is electrolysed for 10 minutes with a current of 1.5 amperes.

What is the mass of copper deposited at the cathode?

Solution:  $t = 10 \times 60 = 600 \text{ s}$

$$Q = I \times t = 1.5 \text{ A} \times 600 \text{ s} = 900 \text{ C}$$

According to the reaction:



We require 2F or  $2 \times 96500 \text{ C}$  to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited

$$= (63 \text{ g mol}^{-1} \times 900 \text{ C}) / (2 \times 96500 \text{ C mol}^{-1})$$

$$= 567 / 1930 \text{ g}$$

$$= 0.2938 \text{ g.}$$

### Products of Electrolysis:

The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to occur. For the occurrence of such reactions some extra potential (called *over potential*) is required.

(i) Electrolysis of molten sodium chloride: During the electrolysis of molten  $\text{NaCl}$ , the products of electrolysis are sodium metal and  $\text{Cl}_2$  gas. The reactions may be expressed as:

At cathode:  $2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}$  (reduction)

At anode:  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$  (oxidation)

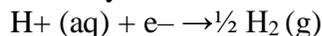
The overall reaction:  $2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$

(ii) Electrolysis of aqueous sodium chloride: During the electrolysis of aqueous sodium chloride solution, the products are  $\text{NaOH}$ ,  $\text{Cl}_2$  and  $\text{H}_2$ .

At the cathode:  $\text{Na}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Na} (\text{s})$   $E^0_{\text{cell}} = -2.71 \text{ V}$

$\text{H}^+ (\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 (\text{g})$   $E^0_{\text{cell}} = 0.00 \text{ V}$

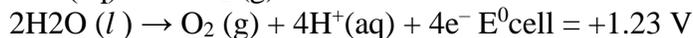
The reaction with higher value of  $E^0$  is preferred and therefore, the reaction at the cathode during electrolysis is:



But  $H^+(aq)$  is produced by the dissociation of  $H_2O$ , i.e.,  $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$

Therefore, the net reaction at the cathode:  $H_2O(l) + e^- \rightarrow \frac{1}{2} H_2(g) + OH^-(aq)$

At the anode:  $Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$   $E^0_{cell} = +1.36 V$



The reaction at anode with lower value of  $E^0$  is preferred and therefore, water should get oxidised in preference to  $Cl^-(aq)$ . However, on account of over potential of oxygen, the reaction  $Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g)$  is preferred. Thus, the net reactions may be summarized as:



At cathode:  $H_2O(l) + e^- \rightarrow \frac{1}{2} H_2(g) + OH^-(aq)$

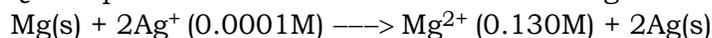
At anode:  $Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$

Net reaction:  $NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g)$



#### ASSIGNMENT:

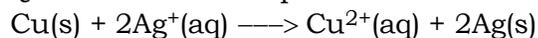
Q1. Represent the cell in which the following reaction takes place:



Calculate its  $E_{(cell)}$  if  $E^0_{(cell)} = 3.17 V$ .

Ans. 2.96 V.

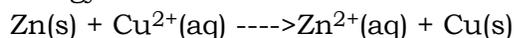
Q2. Calculate the equilibrium constant of the reaction:



$E^0_{(cell)} = 0.46 V$

Ans.  $K_c = 3.92 \times 10^{15}$

Q3. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:



Ans.  $-212.27 \text{ kJ mol}^{-1}$

Q4.

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.

#### Multiple Choice Questions

(1) The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called.....

(a) Cell potential

(b) Cell emf

(c) Potential difference

(d) Cell voltage

(2) Which of the statements about solutions of electrolytes is not correct?

(a) Conductivity of solution depends upon size of ions

(b) Conductivity depends upon viscosity of solution

(c) Conductivity does not depend upon salivation of ions present in solution

(d) Conductivity of solution increases with temperature

(3) The units of cell constant are:

(a)  $\text{ohm}^{-1} \text{cm}^{-1}$

(b) cm

(c)  $\text{ohm}^{-1} \text{cm}$

(d)  $\text{cm}^{-1}$

(4)  $\Lambda^0_m(\text{NH}_4\text{OH})$  is equal to \_\_\_\_\_

(a)  $\Lambda^0_m(\text{NH}_4\text{OH}) + \Lambda^0_m(\text{NH}_4\text{Cl}) - \Lambda^0_m(\text{HCl})$

(b)  $\Lambda^0_m(\text{NH}_4\text{Cl}) + \Lambda^0_m(\text{NaOH}) - \Lambda^0_m(\text{NaCl})$

(c)  $\Lambda^0_m(\text{NH}_4\text{Cl}) + \Lambda^0_m(\text{NaCl}) - \Lambda^0_m(\text{NaOH})$

(d) None of these

(5) In an electrolysis of aqueous Sodium chloride solution which of the half-cell reaction will occur at anode?

(a)  $\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s}) : E^0_{\text{cell}} = -2.71 \text{ V}$

(b)  $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- : E^0_{\text{cell}} = 1.23 \text{ V}$

(c)  $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow 1/2\text{H}_2(\text{g}) : E^0_{\text{cell}} = 0.00 \text{ V}$

(d)  $\text{Cl}^-(\text{aq}) \rightarrow 1/2\text{Cl}_2(\text{g}) + \text{e}^- : E^0_{\text{cell}} = 1.36 \text{ V}$

6The units of molar conductivity are:

(a)  $\text{ohm}^{-1} \text{m}^2 \text{mol}^{-1}$

(b)  $\text{ohm} \text{m}^2 \text{mol}^{-1}$

(c)  $\text{ohm}^{-1} \text{m}^2 \text{mol}$

(d)  $\text{ohm}^{-2} \text{m}^2 \text{mol}^{-1}$

(7) Number of Faradays (F) required to reduce one mole of  $\text{MnO}_4^-$  into  $\text{Mn}^{2+}$  is

(a) 5F

(b) 2F

(c) 1F

(d) 7F

(8) If the  $E^{\circ}_{\text{cell}}$  for a given reaction has a negative value, then which of the following gives the correct relationship for the values of  $\Delta G^{\circ}$  and  $K_{\text{eq}}$ ?

(a)  $\Delta G^{\circ} > 0$ ;  $K_{\text{eq}} > 1$

(b)  $\Delta G^{\circ} < 0$ ;  $K_{\text{eq}} > 1$

(c)  $\Delta G^{\circ} < 0$ ;  $K_{\text{eq}} < 1$

(d)  $\Delta G^{\circ} > 0$ ;  $K_{\text{eq}} < 1$

(9) Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because

(a) Zinc is lighter than iron

(b) Zinc has lower melting point than iron

(c) Zinc has lower negative electrode potential than iron

(d) Zinc has higher negative electrode potential than iron

(10) A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolyzed between platinum electrodes using 0.1 Faraday electricity. How many moles of nickel will be deposited at the cathode?

(a) 0.20

(b) 0.05

(c) 0.10

(d) 0.15

## UNIT 4 CHEMICAL KINETICS

**Chemical Kinetics** the branch of chemistry, which deals with the study of reaction rates and their mechanisms.

**Rate of a Chemical Reaction:** the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. It can be expressed in terms of:

- (i) The rate of decrease in concentration of any one of the reactants.
- (ii) The rate of increase in concentration of any one of the products.

Consider a hypothetical reaction,  $R \rightarrow P$

One mole of the reactant R produces one mole of the product P. If  $[R]_1$  and  $[P]_1$  are the concentrations of R and P respectively at time  $t_1$  and  $[R]_2$  and  $[P]_2$  are their concentrations at time  $t_2$  then,  $\Delta t = t_2 - t_1$ ,  $\Delta[R] = [R]_2 - [R]_1$

$$\Delta [P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R = Decrease in concentration of R / Time taken =  $-\Delta[R]/\Delta t$  (1)

Rate of appearance of P = Increase in concentration of P / Time taken =  $\Delta[P]/\Delta t$  (2)

Since,  $\Delta[R]$  is a negative quantity (as concentration of reactants is decreasing), it is multiplied with  $-1$  to make the rate of the reaction a positive quantity.

Equations (1) and (2) given above represent the average rate of a reaction,  $r_{av}$ .

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur. (Ref. ncert Fig. 4.1)

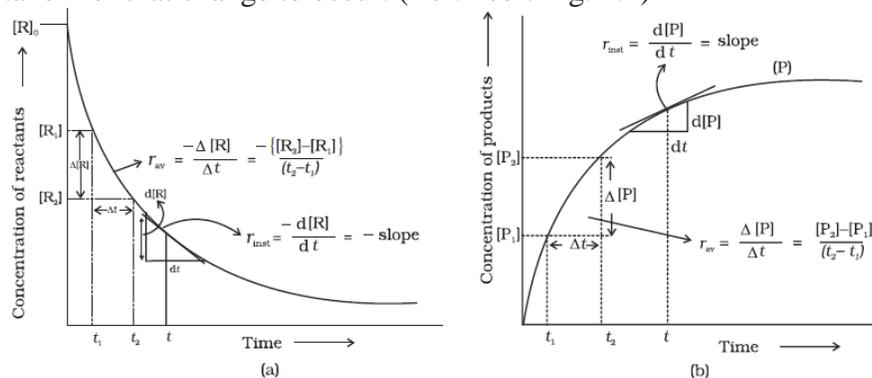


Fig. 4.1: Instantaneous and average rate of a reaction

**Units of rate of a reaction:** The units will be  $\text{mol L}^{-1}\text{s}^{-1}$ .

In gaseous reactions, the units of the rate equation will be  $\text{atm s}^{-1}$ .

**Factors affecting rate of reaction:** The important factors are:

1. Concentration of the reacting species.
2. Temperature of the system.
3. Nature of reactant and products.
4. Presence of a catalyst.
5. Surface area.

## 6. Exposure to radiation.

### Rate Law and Rate Constant:

Consider a general reaction:  $aA + bB \rightarrow cC + dD$

Where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is  $\text{Rate} \propto [A]^x [B]^y$

Where exponents x and y may or may not be equal to the stoichiometric coefficients (a & b) of the reactants. Above equation can also be written as

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

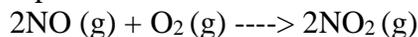
$$-d[R] / dt = k[A]^x [B]^y$$

This form of equation is known as differential rate equation, where *k* is a proportionality constant called **rate constant**.

The equation,  $\text{Rate} = k [A]^x [B]^y$  which relates the rate of a reaction to concentration of reactants is called rate law or rate expression.

**Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.**

For example:



$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

$$-d[\text{R}] / dt = k [\text{NO}]^2 [\text{O}_2]$$

### Order of reaction:

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

x and y indicate the rate is to the change in concentration of A and B.

Sum of these exponents, i.e., x + y in above equation gives the overall order of a reaction.

whereas x and y represent the order with respect to the reactants A and B respectively.

**Order of reaction** is defined as the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction.

A zero-order reaction means that the rate of reaction is independent of the concentration of reactants.

Units of rate constant:

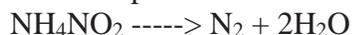
Zero order rate of reaction:  $\text{mol L}^{-1} \text{s}^{-1}$

First order rate of reaction:  $\text{s}^{-1}$

Second order rate of reaction:  $\text{L mol}^{-1} \text{s}^{-1}$

**Molecularity of a reaction:** The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

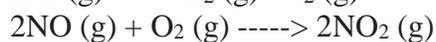
For examples:



Unimolecular reaction



Bimolecular reaction



Trimolecular reaction

Important points of distinction between order and molecularity

S.No.	Order	Molecularity
1	<b>Order</b> is the sum of powers of the concentration terms in the rate law expression.	<b>Molecularity</b> is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
2	Order of a reaction is determined experimentally.	Molecularity is a theoretical concept.
3	Order of a reaction can be zero.	Molecularity of a reaction cannot be zero.

### Integrated rate equations:

**Zero order reaction:** Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.

Consider the reaction,



$$\text{Rate} = -d[R] / dt = k [R]^0$$

$$\text{Rate} = -d[R] / dt = k \times 1$$

$$d[R] = -k dt$$

Integrating both sides

$$[R] = -k t + I \quad (1)$$

Where, I is the constant of integration

At  $t = 0$  the concentration of reactant  $[R] = [R]_0$

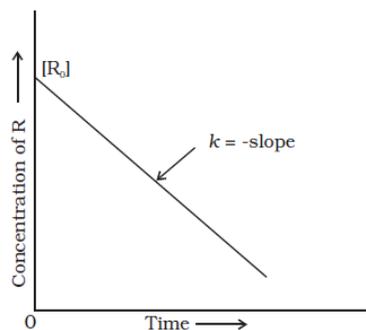
Where  $[R]_0$  is the initial concentration of reactant.

$[R]_0 = -k \times 0 + I = I$ , Substituting the value of I in the equation (1)

$$[R] = -k t + [R]_0$$

$$k = \{ [R]_0 - [R] \} / t$$

Variation in the concentration Vs time plot for a zero-order reaction



Example of Zero order reaction is the decomposition of gaseous ammonia.



$$\text{Rate} = k [\text{NH}_3]^0 = k$$

the rate of the reaction is proportional to the

**First Order Reactions:** The rate of the reaction is proportional to the first power of the concentration of the reactant R.

For example:



$$\text{Rate} = -d[R] / dt = k [R]$$

$d[R] / [R] = -k dt$ , Integrating this equation and we get

$$\ln [R] = -kt + I \quad (1)$$

At  $t = 0$ ,  $\ln [R] = -k \times 0 + I$ ,  
 $I = \ln [R]_0$ , Substituting the value of  $I$  in the equation (1)  
 $\ln [R] = -kt + \ln [R]_0$

$k = \{\ln [R]_0 - \ln [R]\} / t$  Remember that,  $(\log a - \log b = \log(a/b))$

$$k = (1/t) \ln \{[R]_0/[R]\}$$

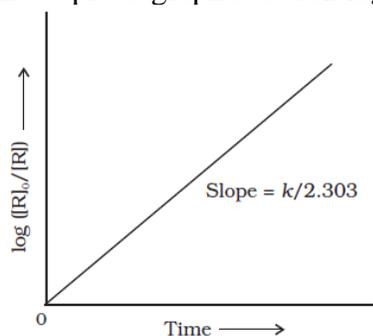
$\ln \{[R]/[R]_0\} = -kt$ , taking antilog both sides

$$[R] = [R]_0 e^{-kt}$$

We know that,  $\ln a = 2.303 \log a$

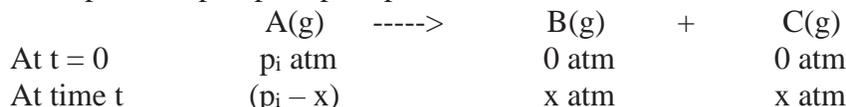
$$k = (2.303/t) \log \{[R]_0/[R]\}$$

If we plot a graph between  $\log [R]_0/[R]$  Vs  $t$ , the slope is  $k/2.303$  for first order reaction



**First order gas phase reaction:**  $A(g) \rightarrow B(g) + C(g)$

Total pressure  $p_t = p_A + p_B + p_C$



$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

$$p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$$

$$k = (2.303/t) \log [p_i/p_A]$$

$$k = (2.303/t) \log [p_i/(2p_i - p_t)]$$

**Half-life of a reaction:** The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as  $t_{1/2}$ .

For a zero order reaction, rate constant is

$$k = \{[R]_0 - [R]\} / t$$

$$\text{At } t = t_{1/2}, [R] = [R]_0 / 2$$

$$k = \{[R]_0 - [R]_0 / 2\} / t_{1/2} = [R]_0 / 2 t_{1/2}$$

$$t_{1/2} = [R]_0 / 2 k$$

For a first order reaction, rate constant is

$$k = (2.303/t) \log \{[R]_0/[R]\}$$

$$\begin{aligned} \text{At } t = t_{1/2}, [\text{R}] &= [\text{R}]_0 / 2 \\ k &= (2.303/t_{1/2}) \log \{ [\text{R}]_0 / [\text{R}]_0 / 2 \} \\ k &= (2.303/t_{1/2}) \log 2 \\ k &= (2.303/t_{1/2}) 0.3010 \end{aligned}$$

$$t_{1/2} = 0.693 / k$$

**For zero order reaction  $t_{1/2} \propto [\text{R}]_0$ .**

**For first order reaction  $t_{1/2}$  is independent of  $[\text{R}]_0$ .**

### Multiple Choice Questions

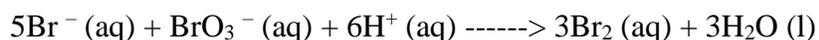
1. Which of the following statements is not correct about order of a reaction?

- (a) The order of a reaction can be a fractional number.
- (b) Order of a reaction is experimentally determined quantity.
- (c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
- (d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

2. Which of the following statements is correct?

- (a) The rate of reaction decreases with passage of time as the concentration of reactant decreases.
- (b) The rate of reaction is same at any time during the reaction.
- (c) The rate of reaction is independent of temperature change.
- (d) The rate of reaction decreases with increase in concentration of reactant.

3. Which of the following expressions is correct for the rate of reaction given below?



- (a)  $\Delta[\text{Br}^-] / \Delta t = 5 \Delta[\text{H}^+] / \Delta t$
- (b)  $\Delta[\text{Br}^-] / \Delta t = 6/5 \Delta[\text{H}^+] / \Delta t$
- (c)  $\Delta[\text{Br}^-] / \Delta t = 5/6 \Delta[\text{H}^+] / \Delta t$
- (d)  $\Delta[\text{Br}^-] / \Delta t = 6 \Delta[\text{H}^+] / \Delta t$

4. Rate law for the reaction  $A + 2B \rightarrow C$  is found to be  $\text{Rate} = k[A][B]$  Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be \_\_\_\_\_

(a) The same

(b) Doubled

(c) Quadruple

(d) Halved

5. The value of rate constant of a pseudo first order reaction \_\_\_\_\_

(a) Depends on the concentration of reactants present in small amount.

(b) Depends on the concentration of reactants present in excess.

(c) Is independent of the concentration of reactants.

(d) Depends only on temperature.

6. If the concentration is expressed in  $\text{mol litre}^{-1}$  and time in second, then the units of rate constant for the first order reactions are

(a)  $\text{Mol litre}^{-1} \text{ s}^{-1}$

(b)  $\text{Mol}^{-1} \text{ litre s}^{-1}$

(c)  $\text{s}^{-1}$

(d)  $\text{Mol}^2 \text{ litre}^{-2} \text{ s}^{-1}$

7. A reaction is found to be of second order with respect to concentration of carbon monoxide. If concentration of carbon monoxide is doubled, the rate of reaction will

(a) Double

(b) Increase by a factor of 4

(c) Triple

(d) Remain unchanged

8. Which of the following statement is not correct for the reaction?  $4A + B \rightarrow 2C + 2D$

(a) The rate of disappearance of B is one-fourth the rate of disappearance of A

(b) The rate of appearance of C is one-half the rate of disappearance of B

(c) The rate of formation of D is one-half the rate of consumption of A

(d) The rate of formation of C and D are equal.

9. For a reaction having rate law expression:  $\text{Rate} = k [\text{A}]^{3/2} [\text{B}]^{-1/2}$  If the concentration of both A and B become four times, the rate of reaction

(a) **Becomes four times**

(b) Becomes 16 times

(c) Decrease four times

(d) Remains same

10. Half-life period of any first order reaction is

(a) Directly proportional to the initial concentration of the reactant

(b) Half of the rate constant

(c) Same for all reactant

(d) **Independent of initial concentration of reactants.**

## UNIT 5 SURFACE CHEMISTRY

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash.

For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases.

**Adsorption:** The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface, is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent.

Adsorption is a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.

**Types of Adsorption:** There are mainly two types of adsorption of gases on solids.

### Physisorption and Chemisorption

If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as **physical adsorption or physisorption**.

When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption or chemisorption**.

### Comparison of Physisorption and Chemisorption

S.No	Physisorption	Chemisorption
1	It arises because of van der Waals' forces.	It is caused by chemical bond formation.
2	It is not specific in nature.	It is highly specific in nature.
3	It is reversible in nature.	It is irreversible.
4	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5	Enthalpy of adsorption is low (20-40 kJ mol <sup>-1</sup> ) in this case.	Enthalpy of adsorption is high (80-240 kJ mol <sup>-1</sup> ) in this case.
6	Low temperature is favourable for adsorption. It decreases with increase of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
7	No appreciable activation energy is needed.	High activation energy is sometimes needed.
8	It depends on the surface area. It increases with an increase of surface area.	It also depends on the surface area. It too increases with an increase of surface area.
9	It results into multimolecular layers on adsorbent surface under high pressure.	It results into Unimolecular layer.

**Factors affecting adsorption of gases on solids:** The extent of adsorption of a gas on a solid surface is affected by the following factors:

1. Nature of the gas
2. Nature of adsorbent
3. Surface area of the adsorbent
4. Effect of temperature

5. Effect of pressure
6. Activation of adsorbent.

**These factors are discussed below:**

1. **Nature of the gas** (or adsorbate): The amount of gas adsorbed by a solid depends on the nature of gas. In general, under given conditions of temperature and pressure, the easily liquefiable gases such as CO<sub>2</sub>, HCl, NH<sub>3</sub>, Cl<sub>2</sub> etc. are adsorbed more than the permanent gases such as H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>. The ease of liquefaction of gas depends upon its critical temperatures (T<sub>c</sub>). The critical temperature of a gas is the minimum temperature above which a gas cannot be liquefied, however high pressure may be applied. The higher the critical temperature, the more easily a gas is liquefied and hence more readily it will be adsorbed because the Vander Waals forces are stronger near the critical temperatures. However, the chemical adsorption is highly specific in nature and a gas gets adsorbed on the solid only if it forms chemical bonds.
2. **Nature of adsorbent:** The extent of adsorption of a gas depends on the nature of adsorbent. Activated charcoal can adsorb gases which are easily liquefied. Many poisonous gases are adsorbed by charcoal. Gases such as H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> are generally adsorbed on finely divided transition metals e.g. Ni and Co. Most common adsorbents used are activated charcoal, finely divided metals, metal oxides (silica gel, aluminium oxide etc.) and clay.
3. **Surface area of the adsorbent:** The extent of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.
4. **Effect of temperature:** The process of adsorption is an exothermic process and is invariably accompanied by evolution of heat. Adsorption will decrease with increase in temperature and Adsorption will be favoured by decrease in temperature.
5. **Effect of pressure:** At a constant temperature, the adsorption of a gas increases with increase in pressure.  
**Decrease of temperature and increase of pressure both tends to increase the extent of adsorption of a gas on a solid.**
6. **Activation of adsorbent:** Activation of adsorbent means increasing the adsorbing power of the adsorbent. To increase the adsorbing power of the adsorbents, they are sub-divided into smaller pieces. As a result, the surface area increases and therefore, the adsorbing power increases.

**Colloidal state:** When the size of the particles is between 10<sup>-9</sup> m (1nm) to 10<sup>-6</sup> m (1000 nm), it behaves like a colloid. **Colloid is not a substance but it is a state of a substance which depends upon the molecular size.**

**Three types of Solutions:**

1. True solutions
  2. Suspensions
  3. Colloidal solutions.
1. **True solution:** True solution is a homogeneous solution which contains small solute particles (molecules or ions) dispersed throughout a solvent. For example, the solution of sodium chloride in water. The particle size is less than 1 nm. The particles

of a solute in a true solution are invisible even under microscope and its particles can pass through ordinary filter paper as well as through animal membrane.

2. **Suspension:** Suspension is a heterogeneous mixture which contains small insoluble particles. The particle size is more than 1000 nm. For example, dirt particles in water. The particles of a suspension may not be visible to naked eye but visible under a microscope. The particles of a suspension can neither pass through an ordinary filter paper nor through animal membrane.
3. **Colloidal solution:** Colloidal solution is a heterogeneous solution which contains particles of intermediate size. The particles of a colloidal solution have diameters 1 to 1000 nm. For example, milk. Such particles cannot be normally seen with a naked eye. The particles of a colloidal solution can pass through an ordinary filter paper but not through animal membrane. Colloidal solutions are intermediate between true solutions and suspensions.

### Phases of colloids and their classification

Colloidal solution is of heterogeneous nature. It consists of two phases i.e., a dispersed phase and a dispersion medium.

1. Dispersed phase: It is the component present in small proportion and is just like a solute in a solution. For example, in the colloidal solution of silver in water, the silver acts as a dispersed phase.
2. Dispersion medium: It is generally Component present in excess and is just like a solvent in a solution. In the above example, water acts as a dispersion medium.

### Classification of Colloids:

Colloids are classified on the basis of the following criteria:

- (i) Physical state of dispersed phase and dispersion medium
- (ii) Nature of interaction between dispersed phase and dispersion medium
- (iii) Type of particles of the dispersed phase.

### 1. Classification based on Physical state of dispersed phase and dispersion medium:

Depending upon the physical state of dispersed phase and dispersion medium whether these are solids, liquids and gases. For examples, solids in liquids –sols, liquids in solids-gels and liquids in liquids-emulsions.

### Types of Colloidal Systems

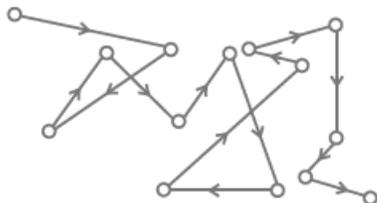
Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	<b>Gas</b>	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, butter
Liquid	<b>Gas</b>	Aerosol	Fog, mist, cloud, insecticide sprays
<b>Gas</b>	Solid	Solid sol	Pumice stone, foam rubber
<b>Gas</b>	Liquid	Foam	Froth, whipped cream, soap lather

2. **Classification based on Nature of interaction between dispersed phase and dispersion medium:** Depending upon Nature of interaction between dispersed phase and dispersion medium, The colloidal solutions can be classified into two types as:
- (i) **lyophilic (solvent attracting)**
  - (ii) **lyophobic (solvent repelling)**
- (i) **Lyophilic colloids:** The colloidal solutions, in which the particles of the dispersed phase have a great affinity for the dispersion medium, are called lyophilic colloids. The word lyophilic means 'liquid loving'. The lyophilic colloids are reversible in nature. The common examples of lyophilic colloids are gum, gelatin, starch, proteins, rubber, etc.
- (ii) **Lyophobic colloids:** The colloidal solutions, in which there is no affinity between particles of the dispersed phase and the dispersion medium, are called lyophobic colloids. The word lyophobic means 'liquid hating'. The lyophobic colloids are irreversible in nature. The common examples of lyophobic colloids are the solutions of metals like Ag and Au, hydroxides like  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ , metal sulphide like  $\text{As}_2\text{S}_3$ , etc.
3. **Classification based on Type of particles of the dispersed phase:** Depending upon Type of particles of the dispersed phase, the colloids are classified as multimolecular, macromolecular and associated colloids.
- (i) **Multimolecular colloids:** On dissolution, a large number of atoms or smaller molecules of a substance (having diameter less than 1 nm) aggregate together to form species having size in the colloidal range (1–1000 nm). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of  $\text{S}_8$  sulphur molecules.
- (ii) **Macromolecular colloids:** These are the substances having big size molecules (called macromolecules) which on dissolution form solution in which the dispersed phase particles have size in the colloidal range. Such substances are called macromolecular colloids. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.
- (iii) **Associated colloids (Micelles):** There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called **micelles**. These are also known as **associated colloids**.  
The formation of micelles takes place only above a particular temperature called **Kraft temperature** ( $T_k$ ) and above a particular concentration called **critical micelle concentration (CMC)**. On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is  $10^{-4}$  to  $10^{-3}$  mol  $\text{L}^{-1}$ . These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

**Properties of colloidal solution:**

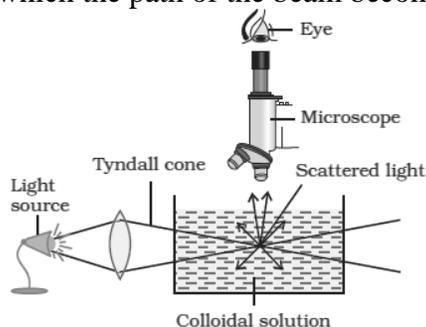
1. **Mechanical properties (Brownian movement)**
2. **Optical properties (Tyndall effect)**
3. **Electrical properties (Electrophoresis)**
4. **Coagulation of colloidal solution.**

1. **Brownian movement:** When colloidal solutions are viewed under a powerful ultra-microscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This type of motion is known as Brownian movement. This motion is independent of the nature of the colloid but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity, faster is the motion.



Brownian movement

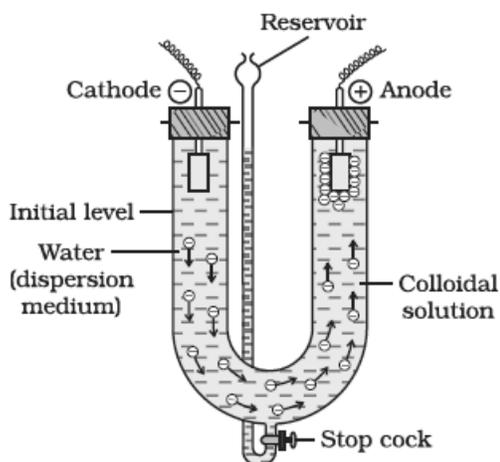
2. **Tyndall effect:** The phenomenon of scattering of light by colloidal particles as a result of which the path of the beam becomes visible is called Tyndall effect.



**Colloidal solution → Show Tyndall effect**  
**True solution → do not show Tyndall effect**

**Lyophilic colloids → do not show Tyndall effect**  
**Lyophobic colloids → Show Tyndall effect**

3. **Electrophoresis:** The phenomenon of movement of colloidal particles under an applied electric field is called Electrophoresis. This can be demonstrated by the following experimental setup (Fig. 5.14).(NCERT)

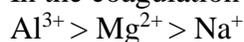


The existence of charge on colloidal particles is confirmed by electrophoresis experiment. When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. Positively charged particles move towards the cathode while negatively charged particles move towards the anode.

4. **Coagulation of colloidal solution:** The phenomenon of precipitation of a colloidal solution by the addition of excess of an electrolyte is called coagulation or flocculation. For example, if  $\text{BaCl}_2$  solution is added to  $\text{As}_2\text{S}_3$  sol, the  $\text{Ba}^{2+}$  ions are attracted by the negatively charged sol particles and their charge gets neutralized. This leads to coagulation.

**Hardy Schulze Rule:** Greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy-Schulze rule.

In the coagulation of a negative sol of  $\text{As}_2\text{S}_3$ , the flocculating power is in the order:



Similarly, in the coagulation of a positive sol  $\text{Fe}(\text{OH})_3$ , the flocculating power is in the order:



It is usually expressed as millimoles per litre. The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller is the coagulating value of an electrolyte, the higher will be the coagulating power of an ion.

For example, for coagulation of negatively charged  $\text{As}_2\text{S}_3$  sol.

$$\frac{\text{Coagulating power of AlCl}_3}{\text{Coagulating power of NaCl}} = \frac{\text{Coagulating value of NaCl}}{\text{Coagulating value of AlCl}_3} = \frac{51}{0.093} \approx 548$$

Thus,  $\text{AlCl}_3$  has 548 times more Coagulating power than  $\text{NaCl}$ .

### Multiple Choice Questions

1. The term 'sorption' stands for \_\_\_\_\_

- (a) Absorption
- (b) Adsorption

(c) Both absorption and adsorption

(d) Desorption

2. Extent of physisorption of a gas increase with \_\_\_\_\_

(a) Increase in temperature

(b) Decrease in temperature

(c) Decrease in surface area of adsorbent

(d) Decrease in strength of Vander Waals forces.

3. Extent of adsorption of adsorbate from solution phase increases with \_\_\_\_\_

(a) Increase in amount of adsorbate in solution

(b) Decrease in surface area of adsorbent

(c) Increase in temperature of solution

(d) Decrease in amount of adsorbate in solution

4. In physisorption, adsorbent does not show specificity for any particular gas because

(a) Involved Vander Waals forces are universal

(b) Gases involved behave like ideal gases

(c) Enthalpy of adsorption is low

(d) It is a reversible process

5. Which of the following is an example of absorption?

(a) Water on silica gel

(b) Water on calcium chloride

(c) Hydrogen on finely divided nickel

(d) Oxygen on metal surface

6. At high concentration of soap in water, soap behaves as \_\_\_\_\_

(a) Molecular colloid

(b) Associated colloid

(c) Macromolecular colloid

(d) Lyophilic colloid

7. Which of the following will show Tyndall effect?

(a) Aqueous solution of soap below critical micelle concentration.

**(b) Aqueous solution of soap above critical micelle concentration.**

(c) Aqueous solution of sodium chloride

(d) Aqueous solution of sugar

8. Freshly prepared precipitate sometimes gets converted to colloidal solution by \_\_\_\_\_

(a) Coagulation

(b) Electrolysis

(c) Diffusion

**(d) Peptization**

9. Which of the following electrolytes will have maximum coagulating value for  $\text{AgI}/\text{Ag}^+$  sol?

(a)  $\text{Na}_2\text{S}$

**(b)  $\text{Na}_3\text{PO}_4$**

(c)  $\text{Na}_2\text{SO}_4$

(d)  $\text{NaCl}$

10. Which of the following process is responsible for the formation of delta at a place where river meet the sea?

(a) Emulsification

(b) Colloid formation

**(c) Coagulation**

(d) Peptization

## UNIT 8 d-AND f-BLOCK ELEMENTS

**General introduction:** The *d*-block of the periodic table contains the elements of the group's 3-12 in which the *d* orbitals are progressively filled in each of the four long periods.

The *f*-block consists of elements in which 4 *f* and 5 *f* orbitals are progressively filled. They are placed in a separate panel at the bottom of the periodic table.

The names *transition metals* and *inner transition metals* are often used to refer to the elements of *d*- and *f*-blocks respectively.

There are mainly four series of the transition metals, 3*d* series (Sc to Zn), 4*d* series (Y to Cd), 5*d* series (La and Hf to Hg) and 6*d* series which have Ac and elements from Rf to Cn.

The two series of the inner transition metals; 4*f* (Ce to Lu) and 5*f* (Th to Lr) are known as *lanthanoids* and *actinoids* respectively.

**Electronic configuration of First Transition Series:** The general electronic configuration of *d*-block elements is  $(n-1) d^{1-10} ns^{0-2}$ . Scandium ( $Z = 21$ ) to Zinc ( $Z = 30$ ) 3*d*-orbitals are gradually filled.

Element	Symbol	At. No.	Electronic configuration
Scandium	Sc	21	[Ar] 3 <i>d</i> <sup>1</sup> 4 <i>s</i> <sup>2</sup>
Titanium	Ti	22	[Ar] 3 <i>d</i> <sup>2</sup> 4 <i>s</i> <sup>2</sup>
Vanadium	V	23	[Ar] 3 <i>d</i> <sup>3</sup> 4 <i>s</i> <sup>2</sup>
Chromium	Cr	24	[Ar] 3 <i>d</i> <sup>5</sup> 4 <i>s</i> <sup>1</sup>
Manganese	Mn	25	[Ar] 3 <i>d</i> <sup>5</sup> 4 <i>s</i> <sup>2</sup>
Iron	Fe	26	[Ar] 3 <i>d</i> <sup>6</sup> 4 <i>s</i> <sup>2</sup>
Cobalt	Co	27	[Ar] 3 <i>d</i> <sup>7</sup> 4 <i>s</i> <sup>2</sup>
Nickel	Ni	28	[Ar] 3 <i>d</i> <sup>8</sup> 4 <i>s</i> <sup>2</sup>
Copper	Cu	29	[Ar] 3 <i>d</i> <sup>10</sup> 4 <i>s</i> <sup>1</sup>
Zinc	Zn	30	[Ar] 3 <i>d</i> <sup>10</sup> 4 <i>s</i> <sup>2</sup>

### General Characteristics of transition elements:

1. Nearly all the transition elements have typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
2. Except mercury which is liquid at room temperature, other transition elements have typical metallic structures.
3. They have high melting and boiling points and have higher heats of vaporization than non-transition elements.
4. The transition elements have very high densities as compared to the metals of groups I and II (*s*-block).
5. The first ionization energies of *d*-block elements are higher than those of *s*-block elements but are lesser than those of *p*-block elements.
6. They are electropositive in nature.
7. Most of them form coloured compounds.
8. They have good tendency to form complexes.
9. They exhibit several oxidation states.
10. Their compounds are generally paramagnetic in nature.
11. They form alloys with other metals.

12. The form interstitial compounds with elements such as hydrogen, boron, carbon, nitrogen etc.
13. Most of the transition metals such as Mn, Ni, Co, Cr, V, Pt etc. and their compounds have been used as good catalysts.

**General Properties of transition elements (first row transition metals):** Metallic character, ionization enthalpy, oxidation states, colour and catalytic property, magnetic properties, interstitial compounds, alloy formation.

1. **Ionic radii:** In general, the ionic radii decrease with increase in oxidation state. For the same oxidation state, the ionic radii generally decrease with increase in nuclear charge.
2. **Metallic character:** All transition elements are metals. The metallic character of transition elements is due to their relatively low ionization enthalpies and number of vacant orbitals in the outermost shell. The hardness of these metals suggests the presence of strong bonding due to overlap of unpaired electrons between different metal atoms. Therefore, these elements exhibit high enthalpies of atomization. In general, the greater number of unpaired d-electrons, greater is the number of bonds and therefore, greater is strength of these bonds.
3. **Ionization enthalpies:** There is an increase in ionization enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals.  
Zinc has high ionization enthalpy because electron has to be removed from 4s orbital of stable ( $3d^{10} 4s^2$ ) configuration.
4. **Oxidation states:** The transition metals exhibit a large number of oxidation states in their compounds. Most of these show variable oxidation states. The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner (n-1) d-electrons in addition to outer ns-electrons because the energies of the ns and (n-1) d-subshells are almost equal. The lower oxidation state is generally shown when only ns-electrons participate in bonding and higher oxidation states are exhibited when both ns and (n-1) d-electrons take part in bonding.

**Different Oxidation States of the first row Transition Metals**

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, +4, +5, +6
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2, +3, +4, +6
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

5. **Formation of Coloured ions:** When an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital, the energy of excitation corresponds to the frequency of light

absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.

#### Colours of Some of the First Row Transition Metal Ions

Ion	Outer configuration	Colour of the ion
Sc(III), Ti(IV)	3d <sup>0</sup>	Colourless
Ti(III)	3d <sup>1</sup>	Purple
V(IV)	3d <sup>1</sup>	Blue
V(III)	3d <sup>2</sup>	Green
V(II), Cr(III)	3d <sup>3</sup>	Violet
Cr(II)	3d <sup>4</sup>	Blue
Mn(III)	3d <sup>4</sup>	Violet
Mn(II)	3d <sup>5</sup>	Pink
Fe(III)	3d <sup>5</sup>	Yellow
Fe(II)	3d <sup>6</sup>	Green
Co(III)	3d <sup>6</sup>	Blue
Co(II)	3d <sup>7</sup>	Pink
Ni(II)	3d <sup>8</sup>	Green
Cu(II)	3d <sup>9</sup>	Blue
Cu(I)	3d <sup>10</sup>	Colourless
Zn(II)	3d <sup>10</sup>	Colourless

6. **Magnetic properties:** When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism* and *Paramagnetism*.

Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted. Substances which are attracted very strongly are said to be ferromagnetic

The magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula

$$\mu = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons and  $\mu$  is the magnetic moment in units of Bohr magneton (BM).

#### Calculated Magnetic Moments (BM)

Ion	Outer configuration	No. of unpaired electrons	Calculate Magnetic moment (BM)
Sc(III)	3d <sup>0</sup>	0	0
Ti(III)	3d <sup>1</sup>	1	1.73
Ti(II)	3d <sup>2</sup>	2	2.84
V(II)	3d <sup>3</sup>	3	3.87
Cr(II)	3d <sup>4</sup>	4	4.90
Mn(II)	3d <sup>5</sup>	5	5.92
Fe(II)	3d <sup>6</sup>	4	4.90
Co(II)	3d <sup>7</sup>	3	3.87
Ni(II)	3d <sup>8</sup>	2	2.84
Cu(II)	3d <sup>9</sup>	1	1.73

Zn(II)	3d <sup>10</sup>	0	0
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**7. Catalytic property:** Many transition metals and their compounds act as good catalysts for various reactions. For example,

- (i) **Iron-molybdenum** is used as a catalyst in the synthesis of ammonia by Haber's process.
- (ii) **Nickel** is used in hydrogenation reactions in organic chemistry.
- (iii) **Vanadium pentoxide, V<sub>2</sub>O<sub>5</sub>** is used for the oxidation of SO<sub>2</sub> to SO<sub>3</sub> in the contact process for the manufacture of H<sub>2</sub>SO<sub>4</sub>.
- (iv) **Manganese dioxide, MnO<sub>2</sub>** is used to catalyze the decomposition of H<sub>2</sub>O<sub>2</sub> solution.
- (v) **Cobalt salts** catalyze the decomposition of bleaching powder.
- (vi) **Pt/Rh** is used in Ostwald process during manufacture of HNO<sub>3</sub>.
- (vii) **Pd** is used in hydrogenation reactions in organic chemistry.

**8. Interstitial compounds:** Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn<sub>4</sub>N, Fe<sub>3</sub>H, VH<sub>0.56</sub> and TiH<sub>1.7</sub>, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as *interstitial* compounds. The principal physical and chemical characteristics of these compounds are as follows:

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

**9. Alloys formation:** Transition metals form a large number of alloys. The alloys formed are hard and have high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non-transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

**Lanthanoids** – The series involving the filling of 4f-orbitals following lanthanum La (Z=57) is called **lanthanoids series**. Cerium, Ce (Z=58) to Lutetium, Lu ((Z=71).

### 1. Electronic configuration of lanthanoids:

Element	Symbol	At. No.	Electronic configuration
Lanthanum	La	57	[Xe] 5d <sup>1</sup> 6s <sup>2</sup>
Cerium	Ce	58	[Xe] 4f <sup>2</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Praseodymium	Pr	59	[Xe] 4f <sup>3</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Neodymium	Nd	60	[Xe] 4f <sup>4</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Promethium	Pm	61	[Xe] 4f <sup>5</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Samarium	Sm	62	[Xe] 4f <sup>6</sup> 5d <sup>0</sup> 6s <sup>2</sup>

Europium	Eu	63	[Xe] 4f <sup>7</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Gadolinium	Gd	64	[Xe] 4f <sup>8</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Terbium	Tb	65	[Xe] 4f <sup>9</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Dysprosium	Dy	66	[Xe] 4f <sup>10</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Holmium	Ho	67	[Xe] 4f <sup>11</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Erbium	Er	68	[Xe] 4f <sup>12</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Thulium	Tm	69	[Xe] 4f <sup>13</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Ytterbium	Yb	70	[Xe] 4f <sup>14</sup> 5d <sup>0</sup> 6s <sup>2</sup>
Lutetium	Lu	71	[Xe] 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>

**Oxidation states:** All lanthanoids exhibit a common stable oxidation state of +3. In addition some lanthanoids show +2 and +4 oxidation states also in solution or in solid compounds.

- (i) Cerium (Ce) and Terbium (Tb) exhibit +4 oxidation states.  
 $\text{Ce}^{4+}$ : [Xe] 4f<sup>0</sup>  
 $\text{Tb}^{4+}$ : [Xe] 4f<sup>7</sup>
- (ii) Europium (Eu) and Ytterbium (Yb) exhibit +2 oxidation states.  
 $\text{Eu}^{2+}$ : [Xe] 4f<sup>7</sup>  
 $\text{Yb}^{2+}$ : [Xe] 4f<sup>14</sup>
- (iii) Lanthanum (La), Gadolinium (Gd) and Lutetium (Lu) exhibit only +3 oxidation states.  
 $\text{La}^{3+}$ : [Xe] 5d<sup>0</sup> 6s<sup>0</sup>  
 $\text{Gd}^{3+}$ : [Xe] 4f<sup>7</sup> 5d<sup>0</sup> 6s<sup>0</sup>  
 $\text{Lu}^{3+}$ : [Xe] 4f<sup>14</sup> 5d<sup>0</sup> 6s<sup>0</sup>

**Lanthanide contraction and its Consequences:** The steady decrease in atomic and ionic sizes of lanthanide elements with increasing atomic number is called Lanthanide contraction.

**Cause of Lanthanide contraction:**

In the lanthanide series, as we move from one element to another, the nuclear charge increases by one unit and one electron is added. The new electrons are added to the same inner 4f-subshells. However, the shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is regular decrease in the sizes with increasing atomic number.

**Consequences of Lanthanide contraction:** The important consequences of Lanthanide contraction are:

1. **Resemblance of second and third transition series:** As a result of Lanthanide contraction, the elements of second and third transition series resemble each other much more than the elements of first and second transition series.
2. **Similarities among lanthanoids:** Because of very small change in radii of lanthanoids, their chemical properties are quite similar. Thus, it is very difficult to separate the elements in pure state.
3. **Basicity differences:** Due to Lanthanide contraction, the size of the lanthanoids ions decreases regularly with increase in atomic number. As a result of decrease in size, their covalent character between lanthanoids ion and OH<sup>-</sup> ions increases from La<sup>3+</sup> to Lu<sup>3+</sup>. Therefore, **the basic strength of the hydroxides decreases with increase in atomic number. Thus, La (OH)<sub>3</sub> is most basic while Lu(OH)<sub>3</sub> is the least basic.**

### Multiple Choice Questions

1. Electronic configuration of a transition element X in +3 oxidation state is  $[\text{Ar}] 3d^5$ . What is its atomic number?

(a) 25

(b) 26

(c) 27

(d) 24

2. The electronic configuration of Cu (II) is  $3d^9$  whereas that of Cu (I) is  $3d^{10}$ . Which of the following is correct?

(a) Cu (II) is more stable

(b) Cu (II) is less stable

(c) Cu (I) and Cu (II) are equally stable

(d) Stability of Cu (I) and Cu (II) depends on nature of copper salts.

3. Which of the following is the correct electronic configuration of gadolinium (At.no.64)?

(a)  $[\text{Xe}] 4f^6 5d^2 6s^2$

(b)  $[\text{Xe}] 4f^7 5d^1 6s^2$

(c)  $[\text{Xe}] 4f^8 6s^2$

(d)  $[\text{Xe}] 4f^9 6s^1$

4. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of  $\text{Cr}^{3+}$  ion is \_\_\_\_\_

(a) 2.87 BM

(b) 3.87 BM

(c) 3.47 BM

(d) 3.57 BM

5. Although Zirconium belongs to 4d transition series and Hafnium to 5d series even then they show similar physical and chemical properties because \_\_\_\_\_

- (a) Both belong to d- orbitals.
- (b) Both have same number of electrons
- (c) Both have similar atomic radius
- (d) Both belong to the same group of the periodic table

6. The effect of lanthanoids contraction in the lanthanoids series of elements by and large means:

- (a) Decrease in both atomic and ionic radii.
- (b) Increase in atomic radii and decrease in ionic radii.
- (c) Increase in both atomic radii and ionic radii.
- (d) Decrease in atomic radii and increase in ionic radii.

7. Which of the following statement is not correct?

- (a)  $\text{La}(\text{OH})_3$  is less basic than  $\text{Lu}(\text{OH})_3$
- (b) In lanthanoids series, ionic radius decreases from  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$
- (c) La is actually an element of transition series rather than lanthanoids.
- (d) Atomic radius of Zr and Hf are same because of lanthanoids contraction.

8. Which one of the following ions exhibits d-d transition and Paramagnetism as well?

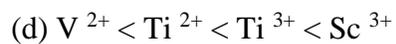
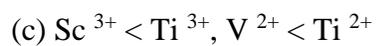
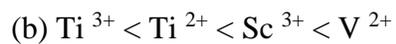
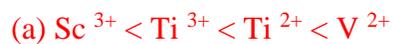
- (a)  $\text{CrO}_4^{2-}$
- (b)  $\text{Cr}_2\text{O}_7^{2-}$
- (c)  $\text{MnO}_4^-$
- (d)  $\text{MnO}_4^{2-}$

9. Iron exhibits +2 and +3 oxidation states. Which of the following statement about iron is incorrect?

- (a) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
- (b) Ferrous compounds are less volatile than the corresponding ferric compounds.
- (c) Ferrous compounds are more easily hydrolyzed than the corresponding ferric compounds.

(d) Ferrous oxide is more basic in nature than the ferric oxide.

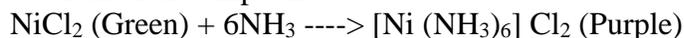
10. Consider the hydrated ions of  $\text{Ti}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Ti}^{3+}$  and  $\text{Sc}^{3+}$ . The correct order of their spin-only magnetic moment is:



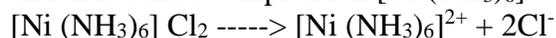
## UNIT 9 COORDINATION COMPOUNDS

**Coordination compounds** are a special class of compounds in which the central metal atom is surrounded by ions or molecules beyond their normal valency. These compounds are widely present in the minerals, plants and animals and play many important functions. Many biologically important compounds are Coordination compounds in which complicated organic species are bound to metal ions. The common examples are: **Haemoglobin** which is a Coordination compound of **Iron**, **Chlorophyll** which is a Coordination compound of **Magnesium** and **Vitamin B<sub>12</sub>** which is a Coordination compound of **Cobalt** etc. The Coordination compounds are also finding extensive applications in metallurgical processes, analytical chemistry, industrial catalysts, textile dyeing, electroplating and medicinal chemistry.

**Coordination compounds** are molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in the solid as well as in the dissolved state. For example, when aqueous ammonia is added to green solution of nickel chloride, NiCl<sub>2</sub>, the colour changes to [Ni (NH<sub>3</sub>)<sub>6</sub>] Cl<sub>2</sub> purple crystals. Such a compound is called Coordination compounds.



When the compound [Ni (NH<sub>3</sub>)<sub>6</sub>] Cl<sub>2</sub> is dissolved in water it ionizes to give a new species. Such an ion is called complex ion [Ni (NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>.



**Coordination compounds** are the compounds in which the central metal atom is bound to a number of anions or neutral molecules by coordinate bonds.

### **Coordination entity and Coordination sphere:**

**Coordination entity:** A coordination entity constitutes a central metal atom or ion bounded to a fix number of oppositely charged ions or neutral molecules. For example, [Co Cl<sub>3</sub> (NH<sub>3</sub>)<sub>3</sub>]

**Coordination sphere:** The central metal atom or ion and the molecules or ions bonded to it are enclosed in a square bracket and a collectively called the **Coordination sphere**.

### **Central atom or ion and Ligands:**

**Central atom or ion:** The atom or ion to which a fixed number of neutral molecules or ions are attached in the coordination entity is called **Central atom or ion**.

**Ligands:** The neutral molecules or ions bonded to the central atom or ion in the coordination entity are called **ligands**. For example,



### **Types of ligands:**

- (i) **Unidentate or monodentate ligands:** When a ligand is bound to a metal ion through a single donor atom, as with Cl<sup>-</sup>, H<sub>2</sub>O or NH<sub>3</sub>, the ligand is said to be **Unidentate ligands**.
- (ii) **Didentate or Bidentate ligands:** When a ligand can bind through two donor atoms as in H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (ethane-1, 2-diamine) or C<sub>2</sub>O<sub>4</sub><sup>2-</sup> (oxalate), the ligand is said to be **Didentate ligands**.
- (iii) **Polydentate ligands:** Ligands having more the two donor atoms present in the molecule, the ligands are said to be **Polydentate ligands**.  
Diethylene triamine acts as **tridentate ligand** having three donor N atoms.  
Triethylene tetra amine acts as **tetradentate ligand** having four donor N atoms.

Ethylenediamine triacetate ion acts as **Pentadentate ligand** having two N atoms and three O atoms.

Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ ) is an important **hexadentate ligand**. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

When a di- or Polydentate ligand uses its two or more donor atoms simultaneously to bind a single metal ion, it is said to be a **chelate ligand**. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing Unidentate ligands.

Ligand which has two different donor atoms and either of the two ligates in the complex is called **ambidentate ligand**.

Examples of such ligands are the  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}_2^-$  ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.

Similarly,  $\text{SCN}^-$  ion can coordinate through the sulphur or nitrogen atom.

**Coordination number:** The total number of ligands attached to a central metal atom or ion is called the Coordination number of that metal atom or ion. For example,

$[\text{Ni}(\text{NH}_3)_4]^{2+}$ : C.N. of  $\text{Ni}^{2+} = 4$

$[\text{CoCl}_3(\text{NH}_3)_3]$ : C.N. of  $\text{Co}^{3+} = 6$

**IUPAC nomenclature of coordination compounds:** Write the IUPAC names of the following coordination compounds:

- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
  - $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
  - $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
  - $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
  - $\text{Hg}[\text{Co}(\text{SCN})_4]$
  - $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$
  - $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]_2(\text{SO}_4)_3$
  - $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$
- Diamminechloridonitrito-N-platinum (II)
  - Potassium trioxalatochromate (III)
  - Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride
  - Pentaamminecarbonatocobalt (III) chloride
  - Mercury (I) tetrathiocyanato-S-cobaltate (III)
  - Triamminetriaquachromium (III) chloride
  - Tris (ethane-1,2-diamine)cobalt(III) sulphate
  - Diamminesilver (I) dicyanidoargentate (I)

**Werner's theory:** Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds such as  $\text{CrCl}_3$ ,  $\text{CoCl}_2$  or  $\text{PdCl}_2$  have primary valence of 3, 2 and 2 respectively.

In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as  $\text{AgCl}$  on adding excess silver nitrate solution in cold but some remained in solution.

1 mol  $\text{CoCl}_3 \cdot 6\text{NH}_3$  (Yellow) gave 3 mol AgCl  
 1 mol  $\text{CoCl}_3 \cdot 5\text{NH}_3$  (Purple) gave 2 mol AgCl  
 1 mol  $\text{CoCl}_3 \cdot 4\text{NH}_3$  (Green) gave 1 mol AgCl  
 1 mol  $\text{CoCl}_3 \cdot 4\text{NH}_3$  (Violet) gave 1 mol AgCl

Werner proposed the term secondary valence for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

#### Formulation of Cobalt (III) Chloride-Ammonia Complexes:

Colour	Formula	Solution conductivity corresponds to
Yellow	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	1:3
Purple	$[\text{CoCl}(\text{NH}_3)_5]^{2+} 2\text{Cl}^-$	1:2
Green	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1
Violet	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1

The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

#### Valence Bond Theory (VBT) for bonding in Coordination Compounds:

The main assumptions of this theory are listed below:

1. The central metal ion in the complex makes available a number of empty orbitals for the formation of coordination bonds with suitable ligands.
2. The number of empty orbitals made available for this purpose is equal to coordination number of the central metal ion. For example, if coordination number is 6, six empty orbitals are made available and if coordination number is 4, four empty orbitals are made available in the central metal ion.
3. The appropriate atomic orbitals (s, p and d) of the metal hybridize to give a set of equivalent orbitals of definite geometry such as square planar, tetrahedral and octahedral and so on.
4. The d-orbitals involved in the hybridization may be either inner d-orbitals i.e. (n-1) d or outer d-orbitals i.e. nd. For example, in case of octahedral hybridization. The orbitals may be two 3d, one 4s and three 4p ( $d^2sp^3$ ) or one 4s, three 4p and two 4d ( $sp^3d^2$ )
5. Each ligand has at least one orbital (of donor atom) containing a lone pair of electrons.
6. The empty hybrid orbitals of metal ion overlap the filled orbitals of the ligand to form metal-ligand coordinate covalent bonds.

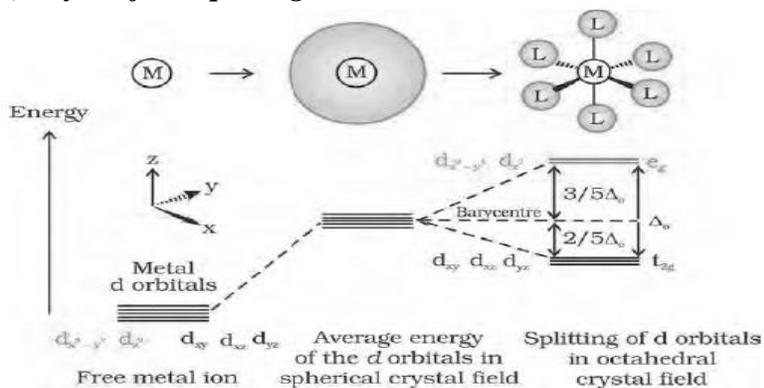
## Number of Orbitals, Types of Hybridizations and Magnetic Properties of Coordination Compounds:

Coordination number	Type of hybridization	Complex/ion	Geometry	No. of unpaired electrons	Magnetic Character
4	$sp^3$	$[\text{NiCl}_4]^{2-}$	Tetrahedral	2	Paramagnetic
4	$dsp^2$	$[\text{Ni}(\text{CN})_4]^{2-}$	Square planar	0	Diamagnetic
6	$sp^3d^2$	$[\text{CoF}_6]^{3-}$	Octahedral	4	Paramagnetic
6	$d^2sp^3$	$[\text{Co}(\text{NH}_3)_6]^{3+}$	Octahedral	0	Diamagnetic

**CRYSTAL FIELD THEORY (CFT):** The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules. The five  $d$  orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.*, they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) in a complex, it becomes asymmetrical and the degeneracy of the  $d$  orbitals is lifted. It results in splitting of the  $d$  orbitals. The pattern of splitting depends upon the nature of the crystal field.

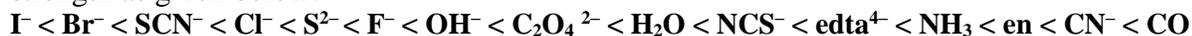
The conversion of five degenerate  $d$ -orbitals of the metal ion into different sets of orbitals having different energies in the presence of electric field of ligand is called **crystal field splitting**.

(a) **Crystal field splitting in octahedral coordination entities:**



**d orbital splitting in an octahedral crystal field (fig. 9.8 ncert)**

**Spectrochemical series:** ligands can be arranged in a series in the order of increasing field strength as given below:



For  $d^4$  ions, two possible patterns of electron distribution arise:

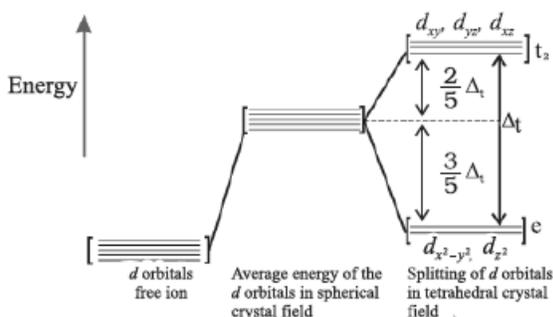
- The fourth electron could either enter the  $t_{2g}$  level and pair with an existing electron, or
- It could avoid paying the price of the pairing energy by occupying the  $e_g$  level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta_o$  and the pairing energy,  $P$  ( $P$  represents the energy required for electron pairing in a single orbital).

The two options are:

(i) If  $\Delta_o < P$ , the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_o < P$  are known as *weak field ligands* and form high spin complexes.

(ii) If  $\Delta_o > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands which produce this effect are known as *strong field ligands* and form low spin complexes.

**(b) Crystal field splitting in tetrahedral coordination entities:**



**d orbital splitting in a tetrahedral crystal field (fig.9.9 ncert)**

In tetrahedral coordination entity formation, the  $d$  orbital splitting (Fig. 9.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that  $\Delta_t = (4/9) \Delta_o$ .

**Colour in Coordination Compounds:** The crystal field theory attributes the colour of the coordination compounds to  $d-d$  transition of the electron.

**Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities:**

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{Co}(\text{CN})_6]^{3-}$	310	Violet	Pale Yellow
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	510	Blue Green	Purple
$[\text{Co Cl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue

### Multiple Choice Questions

1.  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$  exhibits:

(a) Linkage isomerism, ionization isomerism, and geometrical isomerism.

(b) Ionization isomerism, geometrical isomerism, optical isomerism.

(c) Linkage isomerism, geometrical isomerism and optical isomerism.

(d) Linkage isomerism, ionization isomerism and optical isomerism.

2. The crystal field splitting energy of octahedral ( $\Delta_o$ ) and tetrahedral ( $\Delta_t$ ) complexes are related as:

$$\Delta_t = 1/2 \Delta_o$$

$$\Delta_t = 4/9 \Delta_o$$

$$\Delta_t = 3/5 \Delta_o$$

$$\Delta_t = 9/5 \Delta_o$$

3. Sum of coordination number and oxidation number of metal M in the complex  $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$ , (where en is Ethylenediamine) is:

(a) 7

(b) 8

(c) 9

(d) 6

4. In which of the following the number of unpaired electrons is not correct:

(a)  $[\text{CuCl}_4]^{2-}$  : 1 unpaired electron

(b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ : 5 unpaired electrons

(c)  $[\text{Zn}(\text{NH}_3)_2]^{2+}$ : No unpaired electron

(d)  $[\text{CuCl}_4]^{2-}$  : 4 unpaired electrons

5. The coordination number, oxidation number and the number of d-electrons in the metal of the complex  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ , are respectively (atomic number of Co = 27)

(a) 6, 3 and 6

(b) 4, 3 and 6

(c) 6, 6 and 3

(d) 4, 2 and 6

6. Both  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic. The hybridizations of Nickel in these complexes respectively are:

(a)  $\text{sp}^3$  and  $\text{sp}^3$

(b)  $\text{sp}^3$  and  $\text{dsp}^2$

(c)  $\text{dsp}^2$  and  $\text{sp}^3$

(d)  $\text{dsp}^2$  and  $\text{dsp}^2$

7. Which of the following will give maximum number of isomers?

(a)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$

(b)  $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$

(c)  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{en})_2]^{2-}$

(d)  $[\text{Cr}(\text{SCN})_2(\text{NH}_3)_4]^+$

8. Which of the following species is not expected to be a ligand?

(a) Nitric oxide

(b) Ammonium ion

(c) Ammonia

(d) Carbon monoxide

9. Match of the metals (column I) with the coordination compounds/enzymes (Column II)

Column I (Metals)	Column II (Coordination compounds/enzymes)
(a) Co	(i) Wilkinson catalyst
(b) Zn	(ii) Chlorophyll
(c) Rh	(iii) Vitamin B12
(d) Mg	(iv) Carbonic anhydrase

(a) a-ii; b-i; c-iv; d-iii

(b) a-iii; b-iv; c-i; d-ii

(c) a-iv; b-iii; c-i; d-ii

(d) a-i; b-ii; c-iii; d-iv

10. The geometries of the ammonia complexes of  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$  and  $\text{Zn}^{2+}$  respectively are

(a) Octahedral, square planar and tetrahedral

(b) Square planar, octahedral, and tetrahedral

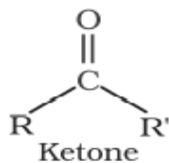
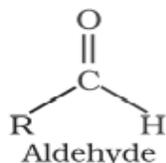
(c) Tetrahedral, square planar and octahedral

(d) Octahedral, tetrahedral and square planar

## UNIT 12 ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

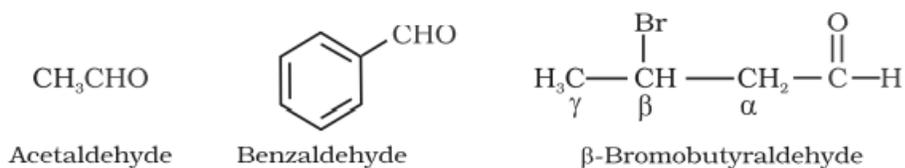
**Aldehydes and Ketones:** The organic compounds containing carbon-oxygen double bond ( $>C=O$ ) called carbonyl group, which is one of the most important functional groups in organic chemistry.

In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones; it is bonded to two carbon atoms.

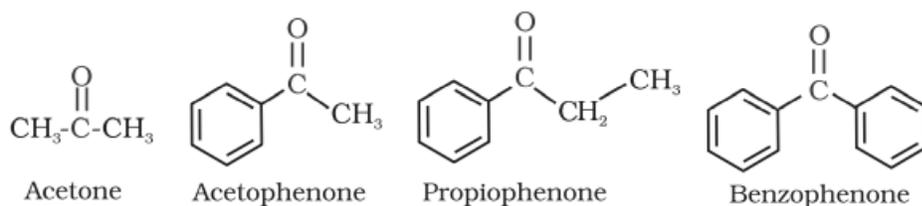


Nomenclature: There are two systems of nomenclature of aldehydes and ketones.

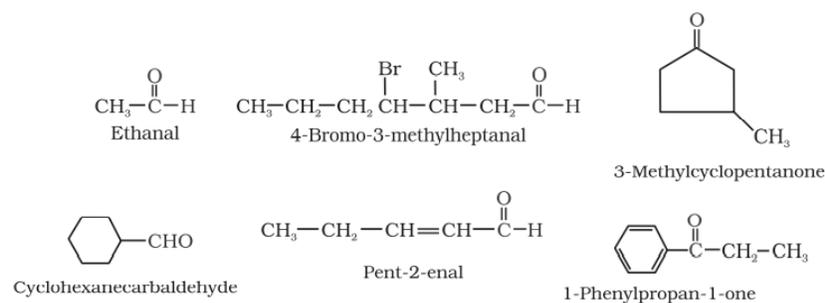
(a) Common names: Acetaldehyde, Benzaldehyde and  $\beta$ -Bromo-butyaldehyde

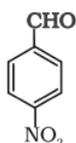
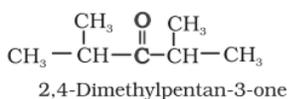
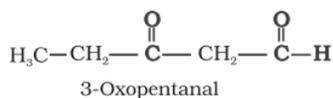


Acetone, Acetophenone, Propiophenone and Benzophenone

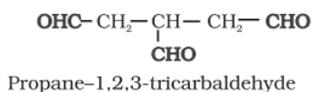


(b) IUPAC names: The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending  $-e$  with  $-al$  and  $-one$  respectively.





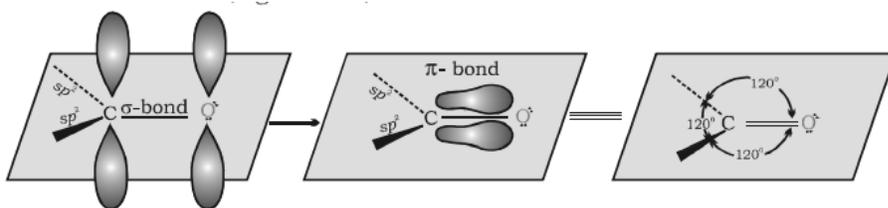
4-Nitrobenzenecarbaldehyde  
or  
4-Nitrobenzaldehyde



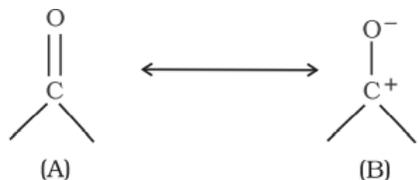
[Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.]

**Structure of the Carbonyl Group:** The carbonyl carbon atom is  $sp^2$ -hybridized and forms three sigma ( $\sigma$ ) bonds. The fourth valence electron of carbon remains in its p-orbital and forms a  $\pi$ -bond with oxygen by overlap with p-orbital of oxygen. In addition, the oxygen atom also has two nonbonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the  $\pi$ -electron cloud is above and below this plane. The bond angles are approximately  $120^\circ$  as expected of a Trigonal coplanar structure.

#### Orbital diagram for the formation of carbonyl group:

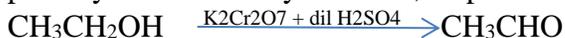


The carbon-oxygen double bond is polarized due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a Nucleophilic (Lewis base) centre. Carbonyl compounds have substantial dipole moments and are polar than ethers. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structure as shown.



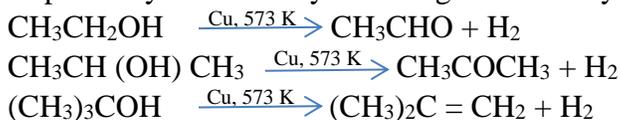
#### Preparation of Aldehydes and Ketones:

1. **By oxidation of alcohols:** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.



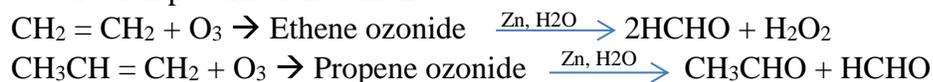
**By dehydrogenation of alcohols:** This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal

catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively and Tertiary alcohol gives 2-methyl propene.

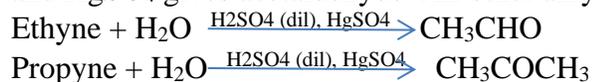


## 2. From hydrocarbons:

(i) By ozonolysis of alkenes: 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.

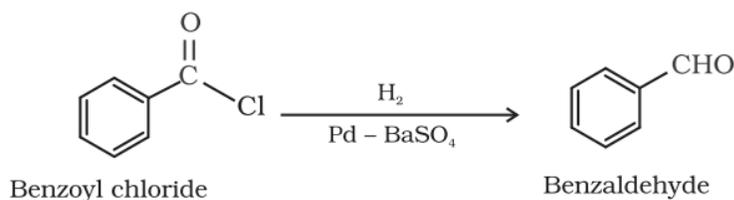


(ii) By hydration of alkynes: Addition of water to Ethyne in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  gives acetaldehyde. All other alkynes give ketones in this reaction.



## Preparation of Aldehydes:

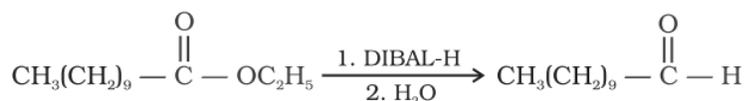
**1. From acyl chloride (acid chloride):** Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund's reduction**.



**2. From nitriles:** 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**.



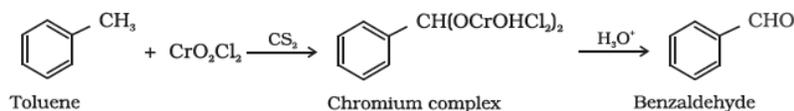
**3. From esters:** Esters are reduced to aldehydes with DIBAL-H.



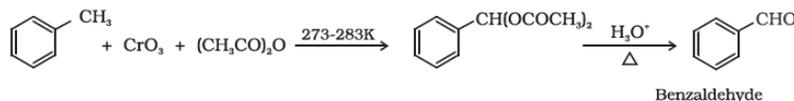
## 4. From hydrocarbons:

(i) By oxidation of methylbenzene

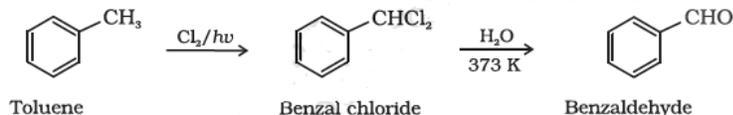
(a) Use of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ): This reaction is called Etard reaction.



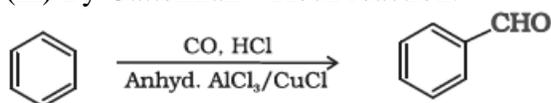
(b) Use of chromic oxide ( $\text{CrO}_3$ ):



(ii) By side chain chlorination followed by hydrolysis:

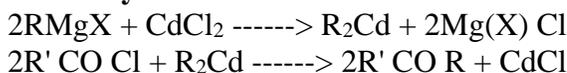


(iii) By Gatterman – Koch reaction:

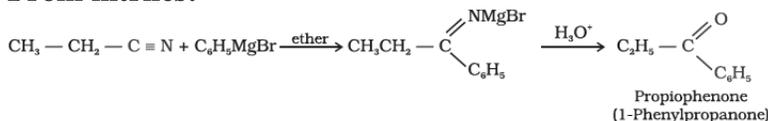


### Preparation of Ketones:

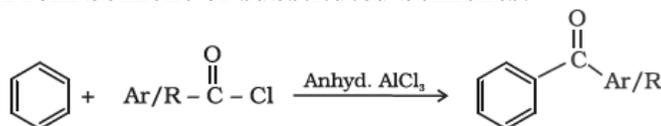
#### 1. From acyl chlorides:



#### 2. From nitriles:



#### 3. From benzene or substituted benzenes:



This reaction is known as Friedel-Crafts acylation reaction.

### 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.

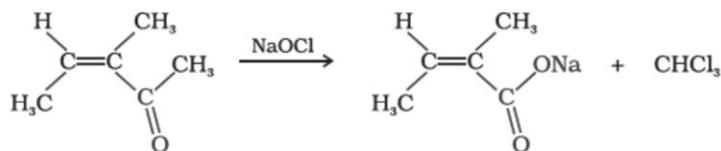
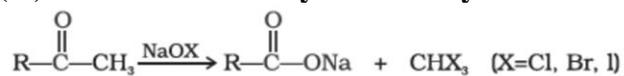
The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. The following compounds of molecular masses 58 and 60 are ranked in order of increasing boiling points.

n-Butane < Methoxyethane < Propanal < Acetone < Propan-1-ol

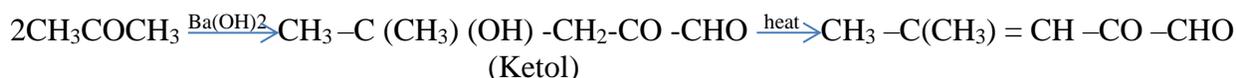
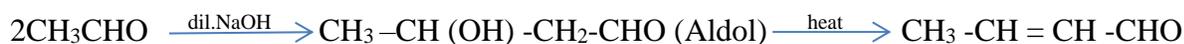




**(iii) Oxidation of methyl ketones by haloform reaction:**



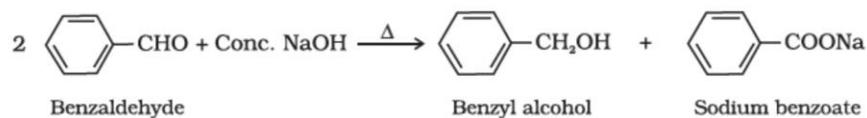
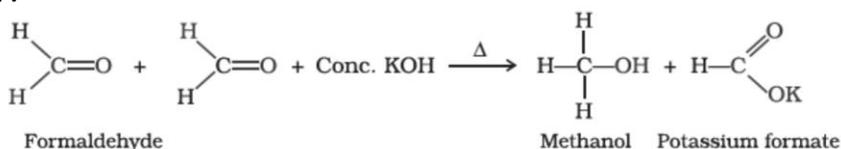
**4. Reactions due to  $\alpha$ -hydrogen:** (i) Aldol condensation: Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form  $\beta$ -hydroxy aldehydes (Aldol) or  $\beta$ -hydroxy ketones (ketol), respectively. This is known as Aldol reaction.



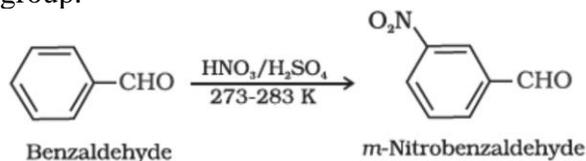
**(ii) Cross Aldol condensation:** When Aldol condensation is carried out between two different aldehydes and / or ketones; it is called cross Aldol condensation.

**5. Other reactions**

**(i) Cannizzaro reaction:**



**(ii) Electrophilic substitution reaction:** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.



**Uses of Aldehydes and Ketones:**

**Formaldehyde** is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products.

**Acetaldehyde** is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.

**Benzaldehyde** is used in perfumery and in dye industries.

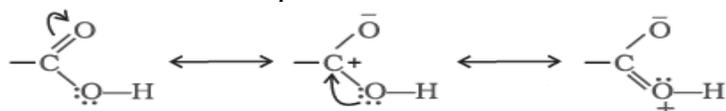
**Acetone and ethyl methyl ketone** are common industrial solvents.

Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

### Carboxylic Acids:

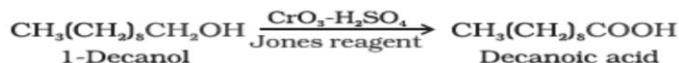
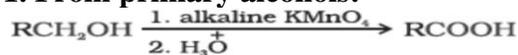
Carbon compounds containing a carboxyl functional group,  $-\text{COOH}$  are called carboxylic acids. The carboxyl group consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl. Carboxylic acids may be aliphatic ( $\text{RCOOH}$ ) or aromatic ( $\text{Ar COOH}$ ) depending on the group, (R, alkyl or Ar, aryl group) attached to carboxylic carbon.

**Structure of Carboxyl Group:** In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about  $120^\circ$ . The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



### Methods of Preparation of Carboxylic Acids:

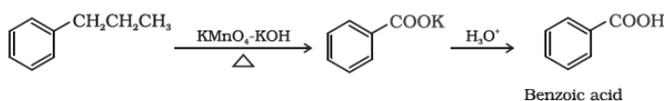
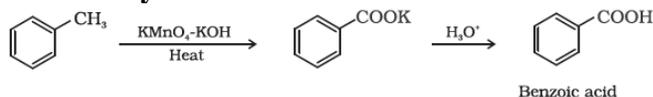
#### 1. From primary alcohols:



#### 2. From aldehydes:



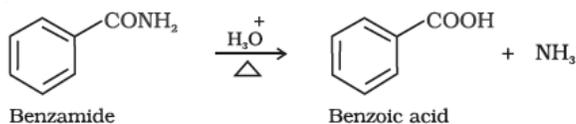
#### 3. From alkyl benzenes:



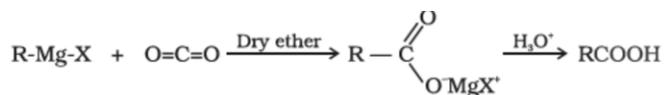
#### 4. From nitriles:



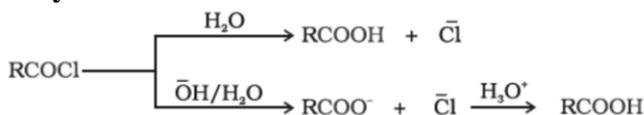
#### 5. From amides:



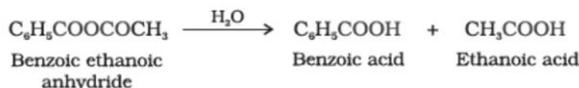
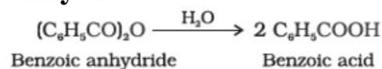
#### 6. From Grignard reagents:



### 7. From acyl halides:



### 8. From anhydrides:



### 6. From esters: Acidic hydrolysis of ethyl benzoate gives benzoic acid.

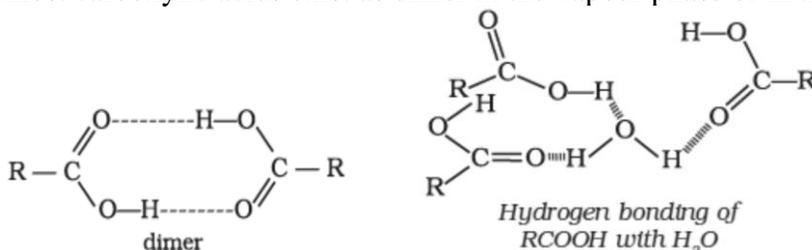


### Physical Properties:

Aliphatic carboxylic acids up to 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 up to 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.

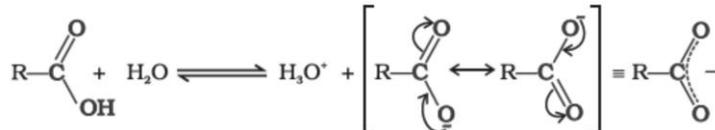
### Chemical Reactions:

#### Reactions Involving Cleavage of O–H Bond:

##### Acidity:



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



For the above reaction:

$$K_{eq} = \frac{[H_3O^+][RCOO^-]}{[H_2O][RCOOH]} \quad K_a = K_{eq} [H_2O] = \frac{[H_3O^+][RCOO^-]}{[RCOOH]}$$

where  $K_{eq}$  is equilibrium constant and  $K_a$  is the acid dissociation constant.

The dissociation constant is called acidity constant. The stronger the acid, the larger will be its  $K_a$  value.

$$pK_a = -\log K_a$$

**Smaller the value of pKa, stronger the acid is.**

The acids have pKa values < 1. Strong acids.

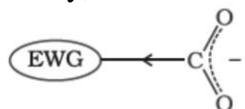
The acids with pKa values between 1 and 5 are considered to be moderately strong acids.

The acids have pKa values between 5 and 15 are extremely weak acids have pKa values >15.

### Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing group's increase the acidity of carboxylic acids by stabilizing the conjugate base through delocalization of the negative charge by inductive and/or resonance effects.

Conversely, electron donating groups decrease the acidity by destabilizing the conjugate base.

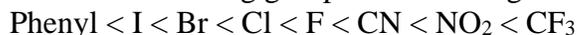


Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



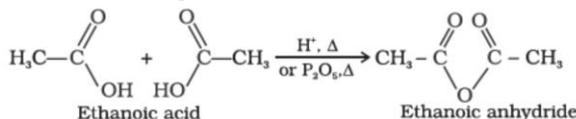
Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is

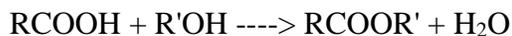


### Reactions Involving Cleavage of C–OH Bond:

#### 1. Formation of anhydride:

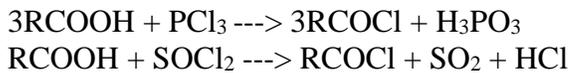


#### 2. Esterification:

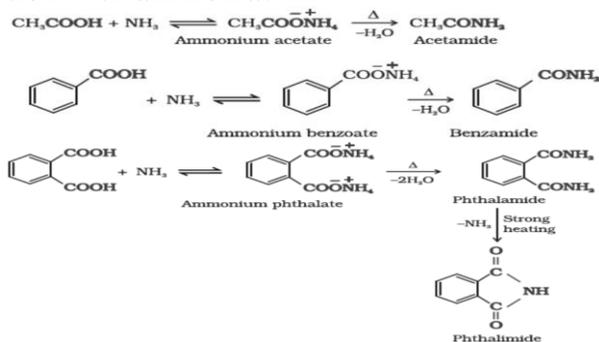


#### 3. Reactions with PCl<sub>5</sub>, PCl<sub>3</sub> and SOCl<sub>2</sub>:



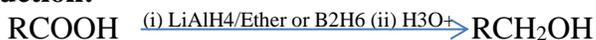


#### 4. Reaction with ammonia:

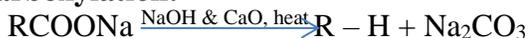


#### Reactions Involving $-\text{COOH}$ Group:

##### 1. Reduction:

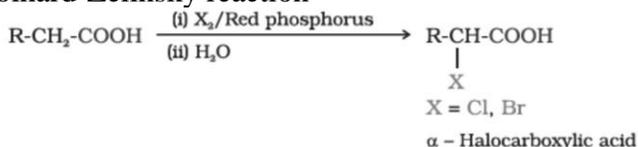


##### 2. Decarboxylation:

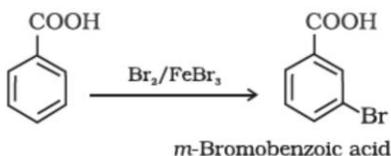
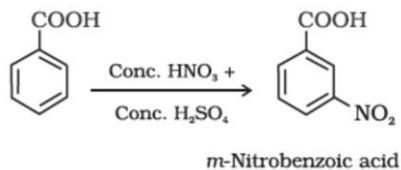


#### Substitution Reactions in the Hydrocarbon Part:

##### Hell-Volhard-Zelinsky reaction



##### 2. Ring substitution:



#### Uses of Carboxylic Acids:

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.

Ethanoic acid is used as solvent and as vinegar in food industry.

Hexanedioic acid is used in the manufacture of nylon-6, 6.

Esters of benzoic acid are used in perfumery.

Sodium benzoate is used as a food preservative.

Higher fatty acids are used for the manufacture of soaps and detergents.

#### Multiple Choice Questions

1. The correct order of increasing acidic strength is
  - (a) Phenol < Ethanol < Chloroacetic acid < Acetic acid
  - (b) Ethanol < Phenol < Chloroacetic acid < Acetic acid
  - (c) Ethanol < Phenol < Acetic acid < Chloroacetic acid**
  - (d) Chloroacetic acid < Acetic acid < Phenol < Ethanol
2. The reagent which does not react with both acetone and benzaldehyde is
  - (a) Sodium hydrogen sulphite
  - (b) Phenyl hydrazine
  - (c) Fehling's solution**
  - (d) Grignard reagent
3. Which of the following compounds will give butanone on oxidation with alkaline  $\text{KMnO}_4$  solution?
  - (a) Butan-1-ol
  - (b) Butan-2-ol**
  - (c) Both (a) and (b)
  - (d) Neither (a) nor (b)
4. In Clemmensen reduction carbonyl compound is treated with
  - (a) zinc amalgam + HCl**
  - (b) sodium amalgam + HCl
  - (c) zinc amalgam + nitric acid
  - (d) sodium amalgam +  $\text{HNO}_3$
5. Which of the following conversions can be carried out by Clemmensen reduction?
  - (a) Benzaldehyde into benzyl alcohol
  - (b) Cyclohexanone into cyclohexane**
  - (c) Benzoyl chloride into benzaldehyde

(d) Benzophenone into diphenyl ethane

6. Benzophenone can be obtained by

(a) benzoyl chloride + benzene +  $\text{AlCl}_3$

(b) benzoyl chloride + diphenyl

(c) benzoyl chloride + phenyl magnesium chloride

(d) benzene + carbon monoxide +  $\text{ZnCl}_2$

7. The product formed by the reaction of an aldehyde with a primary amine is

(a) Carboxylic acid

(b) Aromatic acid

(c) Schiff's base

(d) Ketones

8. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to them

(a) formation of intramolecular H-bonding

(b) formation of carboxylate ion

(c) more extensive association of carboxylic acid via Vander waal's forces of attraction

(d) formation of intermolecular of H- bonding

9. Which of the following reagents may be used to distinguish between phenol and benzoic acid?

(a) Aqueous NaOH

(b) Neutral  $\text{FeCl}_3$

(c) Tollen's reagent

(d) Molisch reagent

10. Which of the following compounds is most reactive towards nucleophilic addition reactions?

(a)  $\text{CH}_3\text{CHO}$

(b)  $\text{CH}_3\text{COCH}_3$

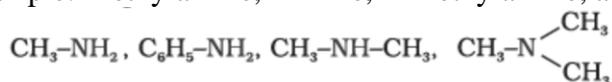
- (c)  $C_6H_5CHO$   
 (d)  $C_6H_5COCH_3$

## UNIT 13 AMINES

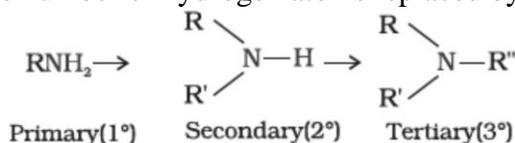
**Amines:** Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

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.

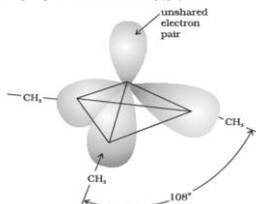
For example: Methylamine, Aniline, Dimethylamine, and Trimethylamine



**Classification:** Amines are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.

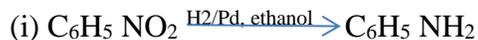


**Structure of Amines:**

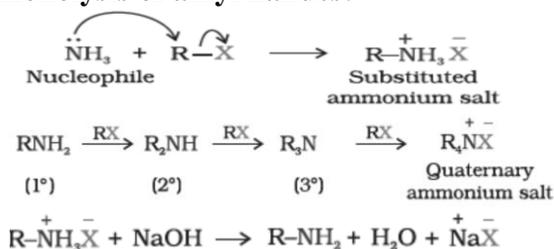


**Preparation of Amines:**

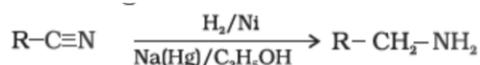
1. Reduction of nitro compounds:



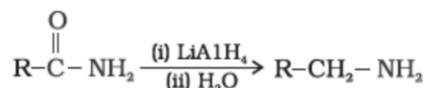
2. Ammonolysis of alkyl halides:



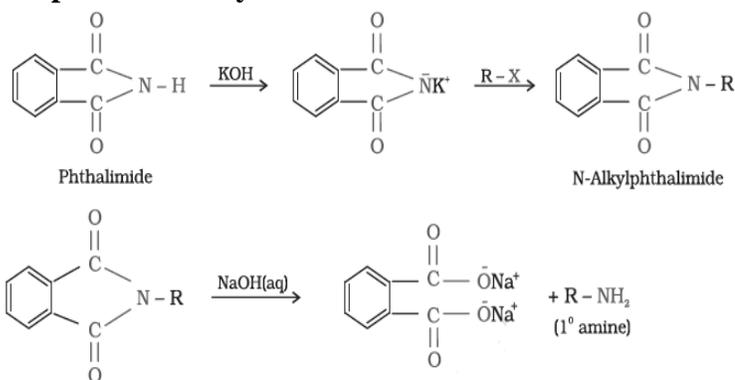
### 3. Reduction of nitriles:



### 4. Reduction of amides:



### 5. Gabriel phthalimide synthesis:



### 6. Hoffmann bromamide degradation reaction:



### Physical Properties:

The lower aliphatic amines are gases with fishy odour.

Primary amines with three or more carbon atoms are liquid and still higher ones are solid.

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part.

Higher amines are essentially insoluble in water.

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

Therefore, the order of boiling points of isomeric amines is as follows:

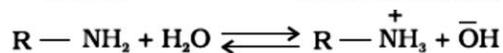
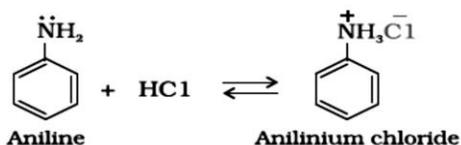
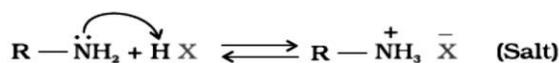
Primary > Secondary > Tertiary

### Boiling Points of Amines of Similar Molecular Masses:

S.No.	COMPOUND	MOLAR MASS	BOILING POINT
1	n-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> (Primary)	73	350.8
2	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH (Secondary)	73	329.3
3	C <sub>2</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> (Tertiary)	73	310.5

### Chemical Reactions:

**1. Basic character of amines:** Amines, being basic in nature, react with acids to form salts.



$$K = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2][H_2O]}$$

$$K_b = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

Larger the value of  $K_b$  or smaller the value of  $pK_b$ , stronger is the base.

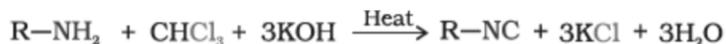
**2. Alkylation:** Amines undergo alkylation on reaction with alkyl halides.



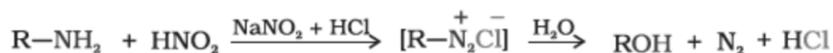
**3. Acylation:** Ethanamine to N-ethyl ethanamide



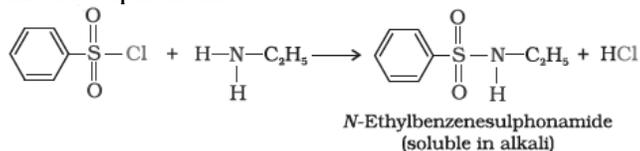
**4. Carbylamine reaction:** Test for primary amines (Aliphatic and aromatic)



**5. Reaction with nitrous acid:**



**6. Reaction with arylsulphonyl chloride:** Benzenesulphonyl chloride ( $C_6H_5SO_2Cl$ ), which is also known as Hinsberg's reagent, reacts with Ethyl amine to form N-Ethylbenzenesulphonamide.

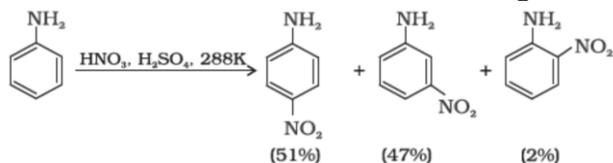


**7. Electrophilic substitution:**

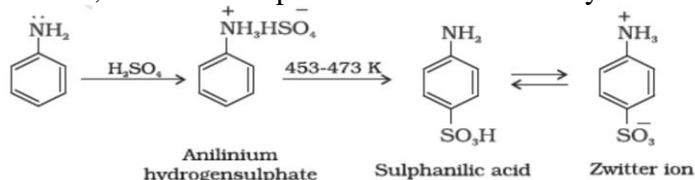
(a) **Bromination:** Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.



**(b) Nitration:** Aniline reacts with nitric acid to give o-, m- & p-nitro aniline.



**(c) Sulphonation:** Aniline reacts with concentrated Sulphuric acid to form anilinium hydrogensulphate which on heating with Sulphuric acid at 453-473K produces p-amino benzene sulphonic acid, known as sulphanilic acid followed by Zwitter ion structure.



**USES OF AMINES:** The important uses of aliphatic and aromatic amines are given below:

1. Aliphatic amines of low molecular mass are used as solvents.
2. Amines are also used as intermediates in drug manufacture and as reagents in organic synthesis.
3. Aromatic amines are used for the manufacture of polymers, dyes and as intermediates for additives in the rubber industry.
4. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.
5. Aromatic amines are converted into arene Diazonium salts which are used for the preparation of variety of aromatic compounds via substitution and coupling reactions.

**Identification of primary, secondary and tertiary amines.**

S.No.	Characteristic reaction	Primary	Secondary	Tertiary
1	Action with nitrous acid (NaNO <sub>2</sub> + HCl)	N <sub>2</sub> is given out with the formation of alcohols.	Nitrosoamines are formed which give Liebermann's Nitroso test.	They remain dissolved forming amine nitrite salt which decomposes on warming to Nitrosoamines and alcohol.
2	Carbylamine reaction (CHCl <sub>3</sub> & alc. KOH)	Give foul smelling Carbylamine.	No reaction	No reaction
3	Acylation	Form amides	Form amides	No reaction

4	Hinsberg's test	Give clear solution which on acidification gives insoluble material	Give insoluble substance which is not affected by acid	Does not react
5	Azo dye test	Give coloured dyes	No reaction	No reaction

### Multiple Choice Questions

1. Which of the following is a 3° amine?

- (a) tert-Butylamine
- (b) 1-Methyl cyclohexylamine
- (c) Triethylamine
- (d) N-methylaniline

2. The correct IUPAC name for  $\text{CH}_2 = \text{CHCH}_2\text{NHCH}_3$  is

- (a) N-methylprop-2-en-1-amine
- (b) allyl methylamine
- (c) 2-amino-4-pentene
- (d) 4-aminopent-1-ene

3. Amongst the following, the strongest base in aqueous medium is

- (a)  $\text{NCCH}_2\text{NH}_2$
- (b)  $(\text{CH}_3)_2\text{NH}$
- (c)  $\text{C}_6\text{H}_5\text{NHCH}_3$
- (d)  $\text{CH}_3\text{NH}_2$

4. Which one of the following amines cannot be prepared by Gabriel phthalimide synthesis?

- (a) Isopropyl amine
- (b) Ethyl methylamine
- (c) Ethylamine
- (d) n-propylamine

5. Which of the following reaction is appropriate for converting 2-phenylpropanamide into 1-phenylethanamine?

- (a) Stephen's reaction
- (b) Hoffmann bromamide reaction
- (c) Carbylamine reaction
- (d) Gabriel phthalimide synthesis

6. Reduction of nitrobenzene by which of the following reagent does not give aniline?

- (a)  $\text{Sn/HCl}$
- (b)  $\text{H}_2\text{-Pd}$
- (c)  $\text{Sn/NH}_4\text{OH}$
- (d)  $\text{Fe/HCl}$

7. The reagent that can be used to convert benzene diazonium chloride to benzene is

- (a)  $\text{H}_3\text{PO}_2$
- (b)  $\text{CH}_3\text{CHO}$
- (c)  $\text{SnCl}_2/\text{HCl}$
- (d)  $\text{LiAlH}_4$

8. Cyclohexylamine and aniline can be distinguished by

- (a) Carbylamine test
- (b) Bromine test
- (c) Beilstein's test
- (d) Hinsberg test

9. The correct order of the basic strength of methyl substituted amines in aqueous solution is

- (a)  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$
- (b)  $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2$
- (c)  $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$
- (d)  $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$

10. The product Y for the reaction:  $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow \text{Y}$

- (a) Phenyl isocyanide
- (b) 2-amino benzaldehyde
- (c) Phenyl cyanide
- (d) 2-amino benzoic acid