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सर्वश्रेष्ठ परीक्षा पथ-प्रदर्शक

B.Sc.
Second Year
(Diploma Course)
Semester-III

CHEMISTRY

SYLLABUS

Chemical Dynamics and Coordination Chemistry

UNIT-I **Chemical Kinetics :** Rate of a reaction, molecularity and order of reaction, concentration dependence of rates, mathematical characteristic of simple chemical reaction – zero order, first order, second order, pseudo order, half-life and mean life. Determination of the order of reaction – differential method, method of integration, half-life method and isolation method.

Theories of Chemical Kinetics : Effect of temperature on rate of reaction, Arrhenius equation, concept of activation energy. Simple collision theory based on hard sphere model, transition state theory (equilibrium hypothesis). Expression for the rate constant based on equilibrium constant and thermodynamic aspect (no derivation).

UNIT-II **Chemical Equilibrium :** Equilibrium constant and free energy, thermodynamic derivation of law of mass action. Le-Chatelier's principle reaction isotherm and reaction isochore-Clapeyron Clausius equation and its applications.

UNIT-III **Phase Equilibrium :** Statement and meaning of the terms-phase, component and degree of freedom, derivation of Gibbs phase rule, phase equilibria of one component system—water, CO_2 and systems. Phase equilibria of two component system—Solid-liquid equilibria, simple eutectic—Bi-Cd, Pb Ag systems.

UNIT-IV **Kinetic Theories of Gases : Gaseous State :** Postulates of kinetic theory of gases, deviation from ideal behaviour, Van der Waals equation of state.

Critical Phenomena : PV isotherms of real gases, continuity of states, the isotherm of Van der Waals equation, relationship between critical constants and Van der Waals constants, the law of corresponding states, reduced equation of state.

Molecular Velocities : Qualitative discussion of the Maxwell's distribution of molecular velocities, collision number, mean free path and collision diameter.

UNIT-V **Liquid State : Liquid State :** Intermolecular forces, structure of liquids (a qualitative description). Structural differences between solids, liquids and gases. Liquid crystals : Difference between liquid crystal, solid and liquid. Classification, structure of nematic and cholesterol phases. **Liquids in solids (gels) :** Classification, preparation and properties, inhibition, general application.

UNIT-VI **Coordination Chemistry :** Werner's theory of coordination complexes, classification of ligands, ambidentate ligands, chelates, coordination numbers, IUPAC nomenclature of coordination complexes (up to two metal centers), Isomerism in coordination compounds, constitutional and stereo isomerism, geometrical and optical isomerism in square planar and octahedral complexes.

UNIT-VII **Theories of Coordination Chemistry :** I. Metal-ligand bonding in transition metal complexes, limitations of valance bond theory, an elementary idea of crystal field theory, crystal field splitting in octahedral, tetrahedral and square planner complexes, John teller effect, factors affecting the crystal-field parameters.

II. Thermodynamic and kinetic aspects of metal complexes : A brief outline of thermodynamic stability of metal complexes, concept of hard and soft acids and bases and factors affecting the stability, stability constants of complexes and their determination, substitution reactions of square planar complexes.

UNIT-VIII **Inorganic Spectroscopy and Magnetism :** I. Electronic spectra of Transition Metal Complexes : Types of electronic transitions, selection rules for d-d transitions, spectroscopic ground states, spectrochemical series, Orgel-energy level diagram for d^1 and d^9 states, discussion of the electronic spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion.
II. Magnetic properties of transition metal complexes, types of magnetic behaviour, methods of determining magnetic susceptibility, spin-only formula, L-S coupling, correlation of μ_s and μ_{eff} values, orbital contribution to magnetic moments, application of magnetic moment data for 3d-metal complexes.

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UNIT-I

Chemical Kinetics

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. What is the unit of rate of a reaction?

Ans. mol $L^{-1}s^{-1}$

Q.2. What is the unit of the rate of a reaction involving gaseous reactants and products?

Ans. atm s^{-1}

Q.3. Express the average rate of the reaction, $H_2(g)+I_2(g)\rightarrow 2HI(g)$, in terms of all reactants and products.

Ans. Average rate $=\frac{-\Delta[H_2]}{\Delta t}=-\frac{\Delta[I_2]}{\Delta t}=\frac{1}{2}\frac{\Delta[HI]}{\Delta t}$

Q.4. Express the instantaneous rate of the reaction, $A+3B\rightarrow 2C+4D$, in terms of all reactants and products.

Ans. Instantaneous rate $=\frac{-d[A]}{dt}=-\frac{1}{3}\frac{d[B]}{dt}=\frac{1}{2}\frac{d[C]}{dt}=\frac{1}{4}\frac{d[D]}{dt}$

Q.5. What type of rate is given by the slope of conc. of reactants *vs* time curve at a particular point?

Ans. Instantaneous rate

Q.6. Why does the rate of a reaction usually increase on increasing the concentration of reactants?

Ans. Due to an increased possibility of molecular collisions.

Q.7. What is the unit of rate constant for a reaction of order n?

Ans. $mol^{1-n}L^{n-1}s^{-1}$

Q.8. Can the order of a reaction be negative?

Ans. Yes

Q.9. What is the order of reaction if the rate law is Rate $=k[A]^{1/2}[B]^2[C]^0$?

Ans. 2.5

Q.10. The reaction, $A+B\rightarrow$ Products, follows the rate law

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

What will be the effect on the rate if the concentration of A is doubled and that of B is halved?

Ans. halved

Q.11. What is the unit of rate constant for a second order reaction?

Ans. $\text{mol}^{-1}\text{Ls}^{-1}$

Q.12. The rate constant of a reaction possesses the units of time^{-1}. What is the order of reaction?

Ans. First

Q.13. For a reaction, $2A \rightarrow A_2$, the rate of reaction becomes three times when the concentration of A is increased 27 times. What is the order of reaction?

Ans. 1/3

Q.14. For the reaction, $A + B \rightarrow$ Products, the rate becomes doubled on doubling the concentration of A but remains unchanged on doubling the concentration of B. What is the rate law?

Ans. Rate $= k[A]$

Q.15. What is the unit of rate constant for a gaseous second order reaction?

Ans. $\text{atm}^{-1}\text{s}^{-1}$

Q.16. The reaction, $A \rightarrow$ Products, is a zero order reaction. To what extent will the rate of the reaction change if the concentration of A is trebled?

Ans. remains unchanged

Q.17. What is the unit of rate constant for a third order reaction?

Ans. $\text{mol}^{-2}\text{L}^2\text{s}^{-1}$

Q.18. The value of rate constant for the reaction, $A \rightarrow$ Products, is 5.6×10^{-3} mol^{-1} Ls^{-1}. How will the rate change when the concentration of A is halved?

Ans. becomes 1/4th

Q.19. How is the half life of a first order reaction related to the concentration of the reaction?

Ans. independent of conc

Q.20. What is the shape of the curve obtained on plotting $\log_{10}[A]$ against t for a first order reaction?

Ans. straight line

Q.21. What will be the order of reaction if the plot of $\log_{10}[A]$ *vs* time is a straight line with a negative slope?

Ans. First

Q.22. How is the slope of the straight line in the plot of $\log_{10} C$ *vs* time for a first order reaction related to the rate constant of the reaction?

Ans. slope $= -\dfrac{k}{2.303}$

Q.23. How is the rate constant of a first order reaction related to the half life of the reaction?

Ans. $k = \dfrac{0.693}{t_{1/2}}$

Q.24. If $[A]_0$ is the initial concentration of a reactant taking part in a first order reaction, how much of the reactant will be left after n half lives?

Ans. $[A]_0/2^n$

Q.25. What is the order of reaction if the plot of rate *vs* $[A]^2$ is a straight line?

Ans. Second.

Q.26. Write the integrated rate equation for a first order reaction.

Ans. $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

Q.27. How is the half life of a reaction of order n related to the initial concentration of the reactant?

Ans. $t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$

Q.28. The plot of log k *vs* X is linear with a slope $= \frac{-E_a}{2.303\,R}$. What is X?

Ans. $\frac{1}{T}$

Q.29. Can the molecularity of a complex reaction be derived from the stoichiometry of the reaction?

Ans. No

Q.30. Which step in a complex reaction does determine the overall rate of the reaction?

Ans. slowest step

Q.31. A reaction proceeds in three steps, one is slow while the other two are fast. Which step will determine the rate of the reaction?

Ans. slow

Q.32. The rate law of a reaction is given by :

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

Which of the following will react fastest?

(a) 1 mol of A and 2 mol of B in 1 L vessel.

(b) 1 mol of A and 1 mol of B in 500 mL vessel.

(c) 3 mol of A and 2 mol of B in 2 L vessel.

Ans. (b); $[A] = 4 \text{ mol L}^{-1}, [B] = 2 \text{ mol L}^{-1}$

$\therefore$ Rate $= k(4)(2)^2$, which is maximum.

Q.33. For a reaction, activation energy $(E_a) = 0$ and rate constant $(k) = 3.2 \times 10^6 \text{ s}^{-1}$ at 300 K. What is the value of the rate constant at 310 K.

Ans. When $E_a = 0$, the rate constant is independent of temperature so that rate constant $(k) = 3.2 \times 10^6 \text{ sec}^{-1}$.

Q.34. The half-life period of a first order reaction is 100 sec. What is rate constant of the reaction?

Ans. $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100\,\text{sec}} = 6.93 \times 10^{-3}\ \text{sec}^{-1}$.

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What are the differences between molecularity and order of reaction.

Ans. **Differences between Molecularity and Order of Reaction**

S. No.	Order of reaction	Molecularity of reaction
1.	It is experimentally determined quantity.	It is theoretical concept.
2.	It is obtained from the rate of the overall reaction.	It is calculated on the basis of the rate determining step.
3.	It may have whole number, zero and even fractional value.	It is always a whole number.
4.	It can not be obtained from balanced or stoichiometric equation.	It can be obtained from balanced equation of single reaction.
5.	It is equal to the sum of the exponents of the molar concentration of the reactants in the rate equation.	It is equal to the minimum number of species (molecule, atom or ions) taking part in a single rate determining step of chemical reaction.
6.	It does not give any information about the reaction mechanism, though it can give some suggestion.	It reveals some fundamental facts about the reaction mechanism.

Q.2. What are zero order reactions? Give their examples and characteristics.

Ans.

Zero Order Reaction

Zero-order reaction is a chemical reaction where in the rate does not vary with the increase or decrease in the concentration of the reactants. Therefore, the rate of these reactions is always equal to the rate constant of the specific reactions (since the rate of these reactions is proportional to the zeroth power of reactants concentration).

Examples of Zero order Reaction

The following reactions are examples of zero order reactions that are not dependent on the concentration of the reactants.

1. The reaction of hydrogen with chlorine (Photochemical reaction).

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\nu} 2HCl_{(g)}$$

2. Decomposition of nitrous oxide over a hot platinum surface.

$$2N_2O \xrightarrow{\text{Pt (hot)}} 2N_2 + O_2$$

3. Iodization of Acetone (In H^+ ion rich medium)

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} ICH_2COCH_3 + HI$$

Reactions wherein a catalyst is required (and is saturated by reactants) are generally zero order reactions. The unit of time rate constant in a zero-order reaction is given by concentration/time or M/s where 'M' is the molarity and 's' refers to one second.

Characteristics of Zero Order Reaction

1. The concentration of reactant decreases linearly with time. $[A]_t = [A]_0 - kt$
2. The time required for the reaction to be complete, *i.e.*, time at which $[A]$ is zero. $t_{\text{completion}} = [A]_0 / k$ = (Initial concentration)/(Rate constant).
3. The units of k are mol lit^{-1} time^{-1}.

Q.3. What are first order reactions? Give their examples and characteristics.

Ans.

First-Order Reaction

A first-order reaction can be defined as a chemical reaction in which the reaction rate is linearly dependent on the concentration of only one reactant. In other words, a first-order reaction is a chemical reaction in which the rate varies based on the changes in the concentration of only one of the reactants. Thus, the order of these reactions is equal to 1.

Examples of First-Order Reactions

$$SO_2Cl_2 \longrightarrow Cl_2 + SO_2$$

$$2N_2O_5 \longrightarrow O_2 + 4NO_2$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Characteristics of First Order Reaction

The characteristics of the first-order reaction are given below :

1. The rate of the reaction is not proportional to the concentration of the reactant.
2. The pace of the reaction is relative to the square of the concentration of the reactant.
3. The rate of the reaction is proportional to the square root of the concentration of the reactant.
4. The pace of reaction is relative to the natural logarithm of the concentration of the reactant.
5. The rate of the reaction is straight forwardly corresponding to the concentration of the reactant.
6. When the concentration of A is increased by 4 times then the rate of the reaction is also increased by 4 times. In general, an increase in the concentration of the reactant by n times increases the rate of the reaction by n times.
7. The time is taken for half the reactant to get reacted, the half-life of the first-order reaction is independent of the concentration. This means that the half-life period of the first-order reaction is constant.

Q.4. What are second order reactions? Give their examples and characteristics.

Ans.

Second Order Reaction

Second order reactions can be defined as chemical reactions wherein the sum of the exponents in the corresponding rate law of the chemical reaction is equal to two. The rate of such a reaction can be written either as $r = k[A]^2$, or as $r = k[A][B]$.

From the rate law equations given above, it can be understood that second order reactions are chemical reactions which depend on either the concentrations of two first-order reactants or the concentration of one-second order reactants.

Since second order reactions can be of the two types described above, the rate of these reactions can be generalized as follows :

$$r = k[A]^x[B]^y$$

Where the sum of x and y (which corresponds to the order of the chemical reaction in question) equals two.

Examples of Second-Order Reactions

A few examples of second-order reaction are given below :

Nigrogen dioxide decomposes into nitrogen monoxide and oxygen. Reaction is given below :

$$2NO_2 \longrightarrow 2NO + O_2$$

Decomposition of hydrogen iodide : Hydrogen iodide breaks down into iodine and hydrogen. The reaction is given below :

$$2HI \longrightarrow I_2 + H_2$$

Decomposition of nitrosyl bromide :

$$2NOBr \longrightarrow 2NO + Br_2$$

Hydrolysis of an ester in presence of a base :

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Combustion reaction : $O_2 + C \longrightarrow O + CO$

Characteristics of a second order reaction (having only one reactant)

1. The rate of the reaction is not proportional to the concentration of the reactant.
2. The rate of the reaction is directly proportional to the square of the concentration of the reactant.
3. The rate of the reaction is directly proportional to the square root of the concentration of the reactant.
4. The rate of the reaction is directly proportional to the natural logarithm of the concentration of the reactant.
5. No determinations of proportionality can be determined from the information provided.

Q.5. What are pseudo-unimolecular reactions? Give their examples.

Ans.

Pseudo-unimolecular Reactions

There are a number of reactions, which follow the first order kinetics though more than one kind of reactants are involved in the reaction. These types of reactions are called pseudo unimolecular reaction.

The example of pseudo unimolecular reaction is the inversion of cane sugar.

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

A second order reaction, in which two reactants are different, is governed by the equation :

$$K = \frac{1}{t\,(a-b)} \ln \frac{b\,(a-x)}{a\,(b-x)}$$

If the concentration of one of the participants is very large compared to that of the other, say $b >> a$, then $b - x \approx b$ and $a - b \approx -b$, which is practically constant.

Hence, the equation reduces to

$$Kb = \frac{1}{t}\ln\frac{a}{(a-x)}$$

Or

$$K^{/} = \frac{1}{t}\ln\frac{a}{(a-x)}$$

That is, under these circumstances, the reaction will follow first order kinetics.

Q.6. What is half life and average life?

Ans.

Half-Life

The half-life of a chemical reaction can be defined as the time taken for the concentration of a given reactant to reach 50% of its initial concentration (*i.e.*, the time taken for the reactant concentration to reach half of its initial value). It is denoted by the symbol '$t_{1/2}$' and is usually expressed in seconds.

Half-Life Formula

It is important to note that the formula for the half-life of a reaction varies with the order of the reaction.

- For a **zero-order reaction**, the mathematical expression that can be employed to determine the half-life is : $t_{1/2} = [R]_0 / 2k$.
- For a **first-order reaction**, the half-life is given by : $t_{1/2} = 0.693 / k$.
- For a **second-order reaction**, the formula for the half-life of the reaction is : $1/k[R]_0$.

Where,

- $t_{1/2}$ is the half-life of the reaction (unit : seconds).
- $[R_0]$ is the initial reactant concentration (unit : mol. L^{-1} or M).
- k is the rate constant of the reaction (unit : $M^{(1-n)}s^{-1}$ where 'n' is the reaction order).

Average life (Ta)

The nuclides of a radioactive substance are disintegrated continously. Some nuclide have very short life (of the order of 10^{-11}) while others have exceedingly long life (of the order of 10^{10} years). Thus, the actual life of radioactive element varies from 0 to ∞. Thus, it is useful to determine the average or mean life of the radioactive substance. It can be defined as follows :

'The ratio of the total life time of all the radioactive nuclei to the total number of nuclei presents at the begining is called the **average or mean life.**'

Thus,

$$\text{Average life, } Ta = \frac{\text{sum of the life times of all the atoms}}{\text{total number of atoms}}$$

From above equation $dN = -\lambda N\,dt$

where dN represents the number of nuclei disintegrating between t and $t + dt$. Each of these nucleus has a life t and hence the sum of the life times of all the nuclei would be $t \cdot dN$. Since, total life time varies from 0 to ∞, hence, for total number of nuclei N_0, one obtains,

$$\text{Total life times of } N_0 \text{ nuclei} = \int_0^{\infty} t\,dN$$

∴

$$Ta = \frac{\text{total life time}}{\text{total number of nuclei}} = \int_0^{\infty}\frac{t\,dN}{N_0}$$

Substituting the value of dN, we have

$$Ta = \int_0^\infty \frac{t\,\lambda\,dt\,N}{N_0} = \int_0^\infty \frac{t\,\lambda\,N_0 e^{-\lambda t}\,dt}{N_0}$$

$$= \lambda \int_0^\infty t\,e^{-\lambda t}\,dt$$

or $$Ta = \frac{1}{\lambda}$$

Thus 'the average life-period (Ta) of a radioactive elements is the reciprocal of the disintegration constant (λ)'.

Relation between $T_{1/2}$ and Ta

From equation $$\lambda = \frac{0.693}{T_{1/2}}$$

Putting this value in above equation, we get

$$Ta = \frac{1}{0.693 / T_{1/2}} = \frac{T_{1/2}}{0.693}$$

or $$Ta = 1.44\ T_{1/2}$$

i.e., the average life is equal to 1.44 times the half life period and the half-life period is equal to 0.693 times the average life.

Q.7. How to find order of reaction?

Ans.

Order of Reaction

Order of reaction is determined by experiment. Although if we know rate law expression determined experimentally then we can determine order of reaction using rate law. Order of reaction can be an integer or fractional value. Following orders of reactions are possible :

- **Order of reaction can be zero :** In zero order reaction the concentration of reactant/s doesn't affect the rate of a reaction.
- **Order of reaction can be negative integer :** Negative integer value of order of reaction indicates that the concentration of the reactants inversely affects the rate of a reaction.
- **Order of reaction can be positive integer :** Positive integer value of order of reaction indicates that the concentration of the reactants directly affects the rate of a reaction.
- **Order of reaction can be fractional value :** Fractional value of order of reaction indicates a more intricate relationship between concentration of reactants and rate of reaction. Generally, complex reactions possess fractional values of order of reaction.

Q.8. Discuss in brief the experimental methods of rate studies.

Ans.

Rate Studies

Many physical and chemical methods are available for studying the reaction rates. Some of them are listed below :

1. **Volume or Pressure Measurement :** When one or more of the components are gases, the reaction rate can be followed by measuring the volume or pressure change. The partial pressures of the species are to be calculated using the reaction stoichiometry.

2. **Titrimetry :** Using acid-base or oxidation-reduction titrations, the reaction course can be followed if atleast one of the components in the reaction is an acid or a base or an oxidising agent or a reducing agent.
3. **Conductometry or Potentiometry :** If one or more of the ions are present or produced in the reaction, suitable methods can be designed based on conductivity or potentiometric measurements.
4. **Spectrophotometry :** When a component of the reaction has a strong absorption band at a particular wavelength region, spectrophotometers could be used for measuring the reaction rate. Photoelectric colorimeters are cheaper instruments and are mainly useful for reaction rate studies in visible region.
5. **Polarimetry :** When atleast one of the components of a reaction is optically active, the reaction rate can be studied from the measurements of optical rotation.

Depending on the reaction under study, the concentration of a reactant or a product is followed at various time intervals using any of the methods mentioned above. These values are then used for calculating the rate constant. Examples are worked out in the next section to illustrate the rate constant calculation. Before studying these examples, we shall discuss the method of arriving at the integrated forms of rate laws.

Q.9. 87.5% of a radioactive substance disintegrates in 40 minutes. What is the half life of the substance.

Ans. Determination of k by substituting the respective values.

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{40}\log\frac{a}{a-0.875a}$$

$$= \frac{2.303}{40}\log\frac{a}{0.125a} = \frac{2.303}{40}\log 8 = 0.051\ \text{min}^{-1}$$

$$\therefore \qquad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.051} = 13.58\ \text{min}$$

Q.10. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^2 sec. What is the rate constant of reaction in sec^{-1}.

Ans.

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$t = 2\times10^2\ \text{sec},\ a = 800\ \text{mol/d}^3,\ (a-x) = 50\ \text{mol/dm}^3$$

$$k = \frac{2.303}{2\times10^2}\log_{10}\frac{800}{50} = 1.386\times10^{-2}\ \text{sec}^{-1}$$

Q.11. The specific rate constant for the second order neutralization of nitropropane by a base is given by

$$\log K = 11.899 - \frac{3169}{T}$$

Where concentration is in moles litre^{-1} and time in minutes. Initial concentration of both reactant is 0.005 M. Calculate E and $t_{1/2}$ at 25°C.

Ans. Arrhenius equation is $\ln K = \ln A - \frac{E}{RT}$

or, $$\log K = \log A - \frac{E}{2.303\,RT}$$

Comparing $$\log K = 11.899 - \frac{3163}{T} \text{ with it we get } \frac{E}{2.303\,R} = 3163$$

or $$E = 2.303 \times 1.987 \times 3163 = 14.5 \text{ K cal}$$

At 25°C $$\log K = 11.899 - \frac{3163}{298} \text{ or } K = 19.2 \text{ litre mole}^{-1}\text{min}^{-1}$$

So, $$t_{1/2} = \frac{1}{Ka} = \frac{1}{19.2 \times 0.005} = 10.4 \text{ min.}$$

Q.12. The activation energy of a gas reaction is 30 Kcal/mole in the temperature range 0° to 60°C. Calculate the approximate temperature co-efficient of the reaction.

Ans. The ratio $\frac{K_{35°C}}{K_{25°C}}$ is approximate temperature co-efficient.

From Arrhenius equation $\ln \frac{K_{35°C}}{K_{25°C}} = \frac{30 \times 10^3}{1.987} \cdot \frac{308 - 298}{308 \times 298}$

So, $$\frac{K_{25°C}}{K_{25°C}} = 5.18$$

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. What do you mean by rate of a chemical reaction? Discuss rate of reaction and rate constant. Also give the units of rate constant.

Ans.

Rate of a Chemical Reaction

We know that chemical reactions are completed with different rates. Some reactions are completed with very fast speed while some take place at slow speed and some at very slow speed. For example, when the aqueous solution of sodium chloride is mixed with the aqueous solution of silver nitrate then the white precipitate of silver chloride is obtained quickly. Similarly, acid base reactions get completed at very fast rate. Generally, these reactions are completed in 10^{-12} to 10^{-16} seconds. On the other hand, some reactions take place at very slow rate like rusting of iron, takes place so slowly that the process cannot be observed generally. Although there are many such reactions which are completed in measurable time and their rate can be studied in laboratory.

For example :

1. Hydrolysis of ester in the presence of sodium hydroxide.

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3CO\bar{O}Na^+ + C_2H_5OH$$

2. Inversion of cane sugar

$$\underset{\text{(Sugar)}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

3. Thermal decomposition of nitrogen pentaoxide

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Such reactions are important from the point of view of chemical kinetics.

We know that the speed of any motor vehicle is expressed in terms of change in its position *i.e.*, distance travelled in definite time interval. Similarly, the speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time.

Consider the following hypothetical reaction :

$$R \longrightarrow P$$

In this R is reactant molecule (1 mole) and P is the product molecule (1 mole). The rate of this reaction can be given by one of the following two ways.

1. The rate of decrease in concentration of reactant R

$$\text{Rate of reaction} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}}$$

2. Rate of increase in the concentration of product P.

$$\text{Rate of reaction} = \frac{\text{Increase in concentration of P}}{\text{Time taken}}$$

If $[R]_1$ and $[P]_1$ are the concentration of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentration at time t_2 then,

$$\Delta t = t_2 - t_1$$
$$\Delta R = [R]_2 - [R]_1$$
$$\Delta P = [P]_2 - [P]_1$$

Where square brackets represents their concentrations and t represents time, ΔR and ΔP denotes the change in concentration of reactant and product respectively. Hence,

$$\text{Rate of reaction} = -\frac{\Delta R}{\Delta t}$$

or

$$\text{Rate of reaction} = +\frac{\Delta P}{\Delta t}$$

Since the concentration of reactants is decreasing therefore negative sign will be used whereas the concentration of products is increasing so positive sign will be used. The change in concentrations of reactants and products with time is obtained according to the curve as shown in the figure 1.

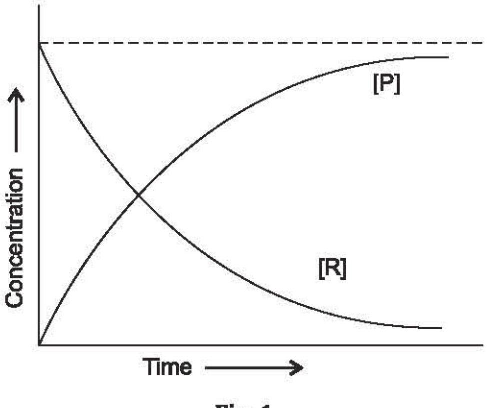


Fig. 1

As the reaction proceeds the rate of reaction decreases exponentially with time. From the curve it is clear that initially the rate of reaction decreases sharply and becomes negligible in the end because the rate time curve runs to infinite distance. Theoretically it means that it will take infinite time to complete a reaction.

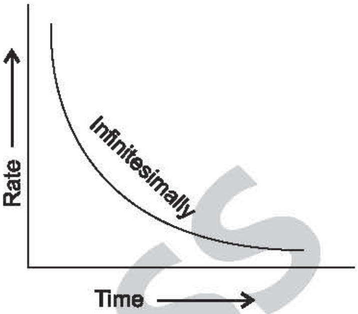


Fig. 2

Initial rate : The rate of reaction in a concentration of reactants-time curve at $t = 0$ is the initial rate of that reaction which is very important in kinetic studies. To determine this a tangent is drawn at $t = 0$ in the curve and slope of that line is determined which is called initial rate.

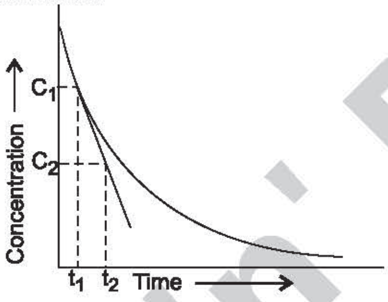


Fig. 3

$$\text{Initial rate} = \tan\theta = -\frac{Dc}{Dt}$$

Rate of Reaction and Rate Constant

According to the law of mass action at a definite temperature the rate of reaction is proportional to the concentration of reactants. Consider the following reaction :

$$A \longrightarrow B$$

If at any moment the concentration of reactant A, is C_A then by the law of mass action,

$$\text{Rate of reaction} = \frac{dx}{dt} \propto [A] \text{ or } \frac{dx}{dt} = K[A] \qquad ...(1)$$

Here K is proportionality constant which depends upon the nature of substances, temperature, etc. It is also called rate constant or rate coefficient or specific rate of reaction, etc. To define the rate constant consider the following reaction :

$$aA + bB + cC \longrightarrow \text{product}$$

Rate of above reaction,

$$\frac{dx}{dt} \propto [A]^a [B]^b [C]^c$$

or

$$\frac{dx}{dt} = K[A]^a [B]^b [C]^c \qquad ...(2)$$

If in above reaction the concentration of all the reactants are same and equal to unity, *i.e.*,

$$[A]^a = [B]^b = [C]^c = 1$$

Then rate of reaction,

$$\frac{dx}{dt} = K \qquad ...(3)$$

Hence specific rate of reaction or rate constant is the rate of any reaction where the concentration of all the reactants is unity. The unit of specific rate of reaction depends upon the order of reaction *i.e.*, the rate constant of reaction is called specific rate of reaction.

Units of Rate Constant

The units of rate constant depend upon the order of reaction, to understand this consider the following reaction :

$$aA + bB + cC \longrightarrow \text{Products}$$

$$\begin{aligned}\text{Rate of reaction} &= \frac{-dx}{dt}\\ &= \frac{\text{change in concentration}}{\text{time taken in change}}\\ &= \text{concentration} \times \text{time}^{-1} \qquad \ldots(1)\end{aligned}$$

$$\begin{aligned}\text{Rate of reaction} &= K[A]^a\,[B]^b\,[C]^c\\ &= K\,[\text{concentration}]^a\,[\text{concentration}]^b\,[\text{concentration}]^c\\ &= K\,[\text{concentration}]^{a+b+c} \qquad \ldots(2)\end{aligned}$$

Equation (1) and (2) are equivalent

$$K\,[\text{concentration}]^{a+b+c} = \text{concentration} \times \text{time}^{-1}$$

$$\Rightarrow \qquad K = \frac{\text{concentration}}{[\text{concentration}]^n} \times \text{time}^{-1}$$

where $n = a + b + c$

$$\Rightarrow \qquad K = [\text{concentration}]^{1-n} \times \text{time}^{-1} \qquad \ldots(3)$$

If the concentration is expressed in gram molecules per litre and time is expressed in second then

$$\textbf{rate constant}\,(\boldsymbol{K}) = \left[\frac{\textbf{mol}}{\textbf{litre}}\right]^{1-n} \times (\textbf{second})^{-1} \qquad \ldots(4)$$

It is an universal relation by which the units of rate constant for any order of reaction can be determined. For example,

1. Units of zero order reaction, $n = 0$

$$k_0 = \left[\frac{\text{mol}}{\text{litre}}\right]^{1-0} \times \text{second}^{-1}$$

The unit of k_0 is mol litre^{-1} second^{-1}

2. Units of first order of reaction; $n = 1$

$$\begin{aligned}k_1 &= \left[\frac{\text{mol}}{\text{litre}}\right]^{(1-1)} \times \text{second}^{-1}\\ &= \left[\frac{\text{mol}}{\text{litre}}\right]^{0} \times \text{second}^{-1} = \text{second}^{-1}\end{aligned}$$

The unit of k_1 is second^{-1}.

3. Unit of second order of reaction, $n = 2$

$$k_2 = \left[\frac{\text{mol}}{\text{litre}}\right]^{(1-2)} \times \text{second}^{-1}$$

$$= \left[\frac{\text{mol}}{\text{litre}}\right]^{-1} \times \text{second}^{-1}$$

$$k_2 = \frac{\text{litre}}{\text{mol}} \text{second}^{-1}$$

The unit of k_2 is litre mol^{-1} sec^{-1}.

Q.2. What do you mean by order and molecularity of reaction. Write the factors affecting the rate of reaction.

Ans.

Order and Molecularity of Reaction

In most of the reactions the molecularity and order of reaction are equal but it is not always true because both are different terms.

Order : "The order of a chemical reaction is defined as the number of atoms or molecules of reactants participating in rate determining step of that reaction." For example :

$$A \rightarrow \text{Product}; \quad \text{rate } r = k_1[A]$$

It is a first order reaction. Similarly,

$$2A \rightarrow \text{Product}; \quad \text{rate } r = k_2[A]^2$$

$$A + B \rightarrow \text{Product}; \quad \text{rate } r = k_2[A][B]$$

These are second order reactions.

Molecularity : The molecularity of a reaction is defined as the number of atoms, molecules or ions by which the stoichiometry of that reaction is represented. For example,

$$A \rightarrow \text{product; molecularity} = 1$$

$$2A \rightarrow \text{product; molecularity} = 2$$

$$A + B \rightarrow \text{product; molecularity} = 2$$

$$3A \rightarrow \text{product; molecularity} = 3$$

$$2A + B \rightarrow \text{product; molecularity} = 3$$

$$A + B + C \rightarrow \text{product; molecularity} = 3$$

So the molecularity of first order reaction is 1, molecularity of second order reaction is 2 and molecularity of third order reaction is 3 but it is not always necessary that the order of reaction is same as the molecularity of that reaction. Molecularity is a whole number which may be more than the order of reaction. Apart from this the order of reaction may also be zero and fraction. The maximum and minimum value of order of a chemical reaction can be 3 and 0 respectively.

It is a clear from the following examples :

1. The reaction between H_2 and Cl_2 on the surface of water in presence of sunlight is a zero order reaction whereas its molecularity is 2.

$$H_2 + Cl_2 \xrightarrow[\text{surface of water}]{h\nu} 2HCl$$

2. Acidic hydrolysis of ester is a first order reaction whereas its molecularity is 2.

$$CH_2COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH \qquad \text{rate} = k_1 [CH_3COOC_2H_5]$$

3. Following reaction is of first order whereas its molecularity is two,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \qquad \text{rate} = k_1 [N_2O_5]$$

Its exaplanation can be done by its mechanism which is as following :

$$N_2O_5 \longrightarrow N_2O_3 + O_2 \qquad \text{(slow step)}$$

$$N_2O_3 \longrightarrow NO + NO_2 \qquad \text{(fast step)}$$

$$N_2O_5 + NO \longrightarrow 3NO_3 \qquad \text{(fast step)}$$

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

In this mechanism first step is slow step which is determining step. The molecularity of slow step is the order of reaction.

Therefore, it is clear that many reactions have identical value of order and molecularity of the reaction whereas it is not true for reactions which are completed in more than one step.

Factors affecting the Rate of Reaction

The rate of reaction is affected by many factors, out of which some important factors are as following :

1. Concentration of the reactants
2. Temperature of the system
3. Nature of reactants and products
4. Presence of catalysts
5. Surface area
6. Exposure to radiation

1. **Concentration of the reactants :** It is observed that the rate of reaction decreases with time. We know that initially the concentration of reactant is maximum therefore the rate of change of concentration will also be maximum. As the concentration of reactant decreases the rate of reaction also decreases. It means that rate of reaction is proportional to the concentration of the reactants.

2. **Temperature of the system :** Generally, on increasing temperature the rate of almost all the reaction increases. In the other words, the rate of reaction decreases on decreasing temperature. This observation is applied on all types of exothermic and endothermic reactions. According to a general approximation, on increasing the temperature of reaction mixture to 10°C the rate of reaction increases two to three times. Its reason is that on increasing temperature the kinetic energy of molecules of reactants also increases and according to collision theory the collision rate on molecules also increases which increases the number of active molecules. This results in the increase in the rate of transformation of reactant molecules into products *i.e.,* the rate of reaction also increases.

3. **Nature of reactants and products :** The rate of reaction is also affected by the nature of reactants and products. In a chemical reaction old bonds break and new bonds are formed. So, the reactivity of substance depends upon the ease of formation and

breaking of some specific bonds. For example, the oxidation of nitric oxide into nitrogen dioxide is completed quickly but the oxidation of carbon monoxide to carbon dioxide is completed slowly.

$$2NO + O_2 \longrightarrow 2NO_2 \qquad \text{(fast rate)}$$

$$2CO + O_2 \longrightarrow 2CO_2 \qquad \text{(slow rate)}$$

In both of these reactions reactant and product molecules seen to be very similar but there is much difference in the rate of reaction.

4. **Effect of catalyst :** Catalysts are those external agents which increase the rate of reaction without making any chemical changes to themselves. It is seen that many reactions get completed with a fast rate in presence of a definite catalyst. For example, the hydrolysis of ester takes place with slow rate in normal conditions but in presence of dilute it takes place with faster rate.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

It is believed that the presence of catalyst reduces the activation energy of the reactants due to which the rate of reaction increases.

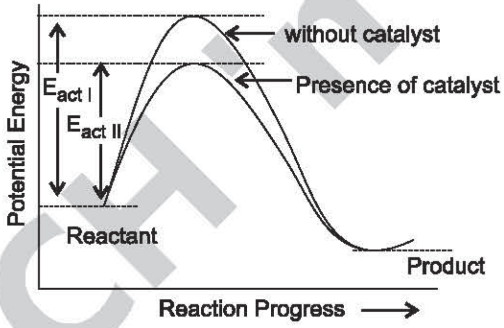


Fig. 4

$E_{\text{act I}}$ = Activation energy without catalyst (more)

$E_{\text{act II}}$ = Activation energy with catalyst (less)

5. **Surface area :** Larger the surface area of reactant higher the rate of reaction. It is obsreved that if reactant is a solid substance then the rate of reaction depends on the size of its particles. More the substance devices in micro particles higher will be the rate of reaction because the surface area of that reactant also increases with the micro division of particles. For example, a larger piece of wood burns slowly but on dividing it in small pieces it burns faster. On increasing the number of pieces it burns faster. On increasing the number of pieces of substance its surface area also increases this results in higher rate of reaction.

6. **Exposure to radiation :** The presence of radiations (visible and UV) abruptly increases the rate of some reactions. The photons of visible and ultoviolet light having high energy quickly dissociated the chemical bonds of reactants due to which the rate of reaction increases, for example, the reaction between H_2 and Cl_2 occurs at a very

slow rate in dark but in presence of sunlight (visible and ultraviolet light) it occurs with an explosion process.

$$H_2 + Cl_2 \xrightarrow{\text{in dark}} 2HCl \text{ (slow rate)}$$

$$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl \text{ (with an explosion)}$$

Q.3. (i) What are zero order reactions? Derive the rate law for zero order reactions. Also give the half life for zero order reactions.

(ii) What are first order reactions? Derive the rate law for first order reactions. Also give the half life for first order reactions.

Ans.

(i) Zero Order Reactions

Those reactions in which the rate of reaction does not depend upon the concentration of reactants are called zero order reactions. *i.e.*, in these reactions the rate of reaction is proportional to the zero power of concentration of reactants. This can be studied as following :

Rate Law : A zero order reaction can be denoted as following :

$$A \xrightarrow{k_0} \text{Product}$$

$$\text{Rate of reaction} = -\frac{d[A]}{dt} = \frac{dx}{dt} \propto [A]^0$$

$$\Rightarrow \qquad \frac{dx}{dt} = k_0[A]^0$$

$$\Rightarrow \qquad \frac{dx}{dt} = k_0 \qquad ...(i)$$

i.e., whatever is the concentration of reactants, the rate remains constant. It is a differential equation.

Integral equation : Equation (i) can also be written as following :

$$dx = k_0 dt \qquad ...(ii)$$

On integrating $\int dx = k_0 \int dt$

$$\Rightarrow \qquad x = k_0 t + C \qquad ...(iii)$$

Where C is an integration constant whose value can be determined by applying initial stages, *i.e.*, at $t = 0, x = 0$ hence $C = 0$

So, from equation (iii) $x = k_0 t$

$$\Rightarrow \qquad \boldsymbol{k_0 = \frac{x}{t}} \qquad ...(iv)$$

It is an integrated rate equation of zero order reaction and k_0 is its rate constant.

Unit : The universal equation of zero order reaction, the unit is following :

$$k_0 = \left(\frac{\text{mol}}{\text{Litre}}\right)^{1-0} \cdot \text{sec}^{-1}$$

The unit of k_0 is mol litre^{-1} sec^{-1}.

Graphical representation : In zer order reaction, the rate equation $x = k_0 t$ is an integrated rate equation. It is equivalent to rate constant k_0.

$$\text{Slope } (\tan\theta) = \frac{\Delta x}{\Delta t} k_0$$

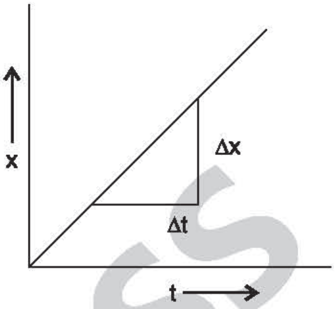


Fig. 5

Half life ($t_{1/2}$) : In a chemical reaction the time taken in decomposition of half of the concentration of reactants is known as half life of that reaction. If the initial concentration of reactants is a then the concentration at $t_{1/2}$ will be $a/2$, hence, from equation (iv),

$$t_{1/2} = \frac{a/2}{k_0} \Rightarrow t_{1/2} = \frac{a}{2k_0} \qquad ...(v)$$

From equation (v), it is clear that the half life of zero order reaction is proportional to the initial concentration of reactants ($t_{1/2} \propto a$).

Some examples of zero order reaction are as following :

1. The reaction between H_2 and Cl_2 on the surface of water in presence of sunlight at constant pressure

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

2. The decomposition of phosphene on the surface of molybdenum at high pressure.

$$2PH_3 \xrightarrow[\text{High pressure}]{M_0} 2P + 3H_2$$

3. Decomposition of ammonia on the surface of tungsten.

$$2NH_3 \xrightarrow[\text{High pressure}]{W} N_2 + 3H_2$$

(ii) First Order Reactions

Those reactions in which the rate of reaction is proportional to the concentration of only one reactant *i.e.*, rate is proportional to the first power of concentration of reactant are called first order reactions.

Rate Law : A first order reaction can be denoted as following :

	$A \longrightarrow$	Product
Initial concentration	a	0
Concentration at time (t)	$(a-x)$	x
	mol/litre	mol/litre

According to above the initial concentration of A (at $t = 0$) is a mol/litre which reduces to $(a - x)$ after time t whereas the product obtained will be x mol/litre.

By the law of mass action,

Rate of reaction

$$\left(\frac{dx}{dt}\right) = -\frac{d(a-x)}{dt} = -\frac{d[A]}{dt} \propto (a-x) \qquad ...(i)$$

i.e.,

$$\frac{dx}{dt} = K_1(a-x) \qquad ...(ii)$$

Where k_1 is the rate constant of first order reaction and equation (ii) is the differential equation of rate of first order reaction.

Integrated Rate Equation : On intergrating equation (ii),

$$\int \frac{dx}{(a-x)} = k_1 \int dt \qquad \left(\because \int \frac{dx}{x} = \ln|x|\right)$$

$$-\ln(a-x) = k_1 t + C \qquad \text{...(iii)}$$

Initially at $t = 0, x = 0$ therefore,

$$-\ln a = C \qquad \text{...(iv)}$$

From equation (iii) and (iv),

$$-\ln(a-x) = k_1 t - \ln a$$

$$\Rightarrow \quad \ln a - \ln(a-x) = k_1 t$$

$$\Rightarrow \quad k_1 t = \ln \frac{a}{a-x} \qquad \text{...(v)}$$

$$\Rightarrow \quad k_1 t = 2.303 \log \frac{a}{a-x}$$

$$\Rightarrow \quad \boldsymbol{k_1 = \frac{2.303}{t} \log \frac{a}{(a-x)}} \qquad \text{...(vi)}$$

It is the integrated rate equation of first order.

Interval Equation : If the initial concentration of reactant A is unknown then interval formula can be used to determine the rate constant. In this formula initial concentration is removed from the rate equation. Let x_1 and x_2 amounts of reactant have decomposed at times t_1 and t_2 respectively. Equation (vi) can be written as following :

$$t_1 = \frac{2.303}{k_1} \log \frac{a}{(a-x_1)} \qquad \text{...(vii)}$$

$$\Rightarrow \quad t_2 = \frac{2.303}{k_1} \log \frac{a}{(a-x_2)} \qquad \text{...(viii)}$$

Subtracting equation (vii) from equation (viii)

$$t_2 - t_1 = \frac{2.303}{k_1}\left[\log \frac{a}{(a-x_2)} - \log \frac{a}{(a-x_1)}\right]$$

$$\Rightarrow \quad t_2 - t_1 = \frac{2.303}{k_1} \log \frac{a-x_2}{a-x_1} \qquad \text{...(ix)}$$

Graphical representation : We can draw many curves for first order reaction. The kinetic equation of first order reaction :

$$t = \frac{2.303}{k_1} \log \frac{a}{a-x}$$

$$\Rightarrow \quad \log \frac{a}{a-x} = \frac{k_1}{2.303} t \qquad \text{...(x)}$$

If a graph is drawn between $\log \frac{a}{a-x}$ and t then the straight line $(y = mx)$ passing from origin point is obtained and the slope will be :

$$\tan\theta = \frac{k_1}{2.303} \qquad ...(xi)$$

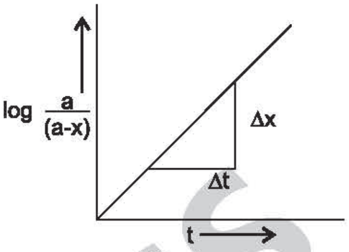


Fig. 6

Rate constant can be estimated easily with the help of above formula.

Equation (x) can also be written as following :

$$\log a - \log(a-x) = \frac{k_1}{2.303} t$$

But log a is a constant quantity therefore,

$$\log(a-x) = -\frac{k_1}{2.303} t + \log a \qquad ...(xii)$$

It is the straight line $(y = -mx + c)$ having opposite slope and intercept at y-axis as shown in figure *i.e.*, in curve between $\log(a-x)$ and t.

The slope of this straight line will be as following by which the value of k_1 can be calculated.

$$\tan\theta = \frac{\Delta Y}{\Delta t} = -\frac{k_1}{2.303}$$

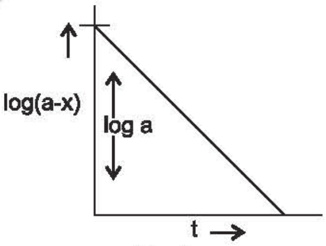


Fig. 7

Curve can also be drawn by interval formula.

$$\log\frac{a-x_1}{a-x_2} = \frac{k_1}{2.303}(t_2 - t_1)$$

...(xiii)

Its slope, $\tan\theta = \frac{k}{2.303}$

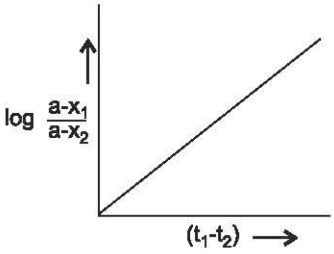


Fig. 8

Half life $(t_{1/2})$: If the initial concentration of reactants is a gram mol per litre then the time is concentration to $a/2$ is called half life. Therefore by kinetic equation

$$\Rightarrow \quad t_{1/2} = \frac{2.303}{k_1}\log\frac{a}{a-(a/2)}$$

$$\Rightarrow \quad t_{1/2} = \frac{2.303}{k_1}\log(2)$$

$$\Rightarrow \quad t_{1/2} = \frac{2.303 \times 0.3010}{k_1} \qquad (\because \log 2 = 0.3010)$$

Hence, $$t_{1/2} = \frac{0.693}{k_1} \qquad ...(xiv)$$

It represents the half life of first order reaction. From half life equation it is clear that half life of first order reaction depends upon the initial concentration of the reactants.

Unit : By the universal relation for the determination of rate constant we know that :

$$\text{Unit of } k_1 = \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \sec^{-1}$$

$$\text{Unit of } k_1 = \sec^{-1} \qquad (\because n = 1)$$

Examples of first order reaction can be given as following :

1. On heating the aqueous solution of ammonium nitrate :

$$NH_4NO_2 \xrightarrow{\Delta} 2H_2O + N_2$$

2. Thermal decomposition of azoisopropane :

$$(CH_3)_2CH{-}N{=}N{-}CH(CH_3)_2 \xrightarrow{\Delta} N_2 + C_6H_{14}$$

3. All radioactive decay are first order reactions.

Q.4. What are second order reactions? Derive the rate law for second order reaction? Also give the half life for second order reactions.

Ans.

Second order reactions

Second order reaction can be defined as chemical reactions where in the sum of the exponents in the corresponding rate law of the chemical reaction is equal to two.

(a) **Rate law second order reaction (initial species is same) :** Let us consider a reaction :

$$2A \longrightarrow \text{Product}$$

If this reaction follow a second order rate law, then we can write a rate expression :

$$-\frac{dC_A}{dt} \propto C_A^2$$

where, C_A is the concentration of the reactant A at time t.

or

$$-\frac{dC_A}{dt} = kC_A^2 \ (k \text{ is the rate constant})$$

$$-\frac{dC_A}{C_A^2} = kdt$$

$$-\int_{(C_A)_0}^{C_A} \frac{dC_A}{C_A^2} = k\int_0^t dt$$

$$\frac{1}{C_A} - \frac{1}{(C_A)_0} = kt$$

$$\frac{1}{C_A} = \frac{1}{(C_A)_0} + kt$$

If we plot this rate expression in a graph $\frac{1}{C_A}$ *vs* t, we will get a straight line graph with a slope (k) and it will cut y axis at $\frac{1}{(C_A)_0}$.

Rate constant : We derived the second order rate law and from this rate expression second order rate constant can be derived.

$$\frac{(C_A)_0 - C_A}{C_A \cdot (C_A)_0} = kt$$

$$k = \frac{1}{t}\frac{(C_A)_0 - C_A}{C_A \cdot (C_A)_0}$$

So, unit of rate constant k will be

$$\text{unit} = \frac{\text{concentration}}{\text{concentration} \cdot \text{concentration} \cdot \text{time}}$$

$$= \frac{1}{\text{concentration} \cdot \text{time}} = \text{mol}^{-1} \cdot \text{lit} \cdot \text{sec}^{-1}$$

Half life of a second order reaction : So, when $t = t_{1/2}$, then $C_A = \frac{(C_A)_0}{2}$.

So, the expression of half life will be

$$\frac{2}{(C_A)_0} - \frac{1}{(C_A)_0} = kt_{1/2}$$

$$\frac{1}{(C_A)_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{2 \cdot (C_A)_0}$$

Like the first order rate law, second order rate law can be expressed in other format where the initial concentration of reactant is 'a mol/litre' and at any time t, the concentration is $(a - x)$ mol/litre where x is the amount of reactant already reacted at time t.
So, the first order rate law can be written by replacing $C_A = (a - x)$ and $(C_A)_0 = a$

$$\frac{1}{a - x} - \frac{1}{a} = kt$$

$$\frac{a}{a(a - x)} = kt$$

$$k = \frac{1}{t}\frac{a}{a(a - x)}$$

(b) **Second order reaction (initial species are different) :** Let us see another type of second order reaction :

$$A + B \longrightarrow \text{Product}$$

The initial concentration of A and B is a and b mol/lit respectively. At any time t, x mol/lit of each reactant have converted to product. So, at time t, the remaining concentration of A and B is $(a - x)$ and $(b - x)$ mol/lit respectively. Now with respect to product concentration (x mol/lit), the second order rate of the above reaction can be written as

$$\frac{dx}{dt} = k(a - x)(b - x)$$

$$\frac{dx}{(a-x)(b-x)} = kdt$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = k\int_0^t dt$$

$$\frac{-1}{a-b}\int_0^x \left[\frac{1}{(a-x)} - \frac{1}{(b-x)}\right] dx = k\int_0^t dt$$

$$\frac{1}{a-b}[\ln(a-x) - \ln(b-x)]_0^x = kt$$

$$\frac{1}{a-b}([\ln(a-x) - \ln a] - [\ln(b-x) - \ln b]) = kt$$

$$\frac{1}{a-b}\left[\ln\frac{(a-x)}{a} - \ln\frac{(b-x)}{b}\right] = kt$$

$$\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = kt$$

$$k = \frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

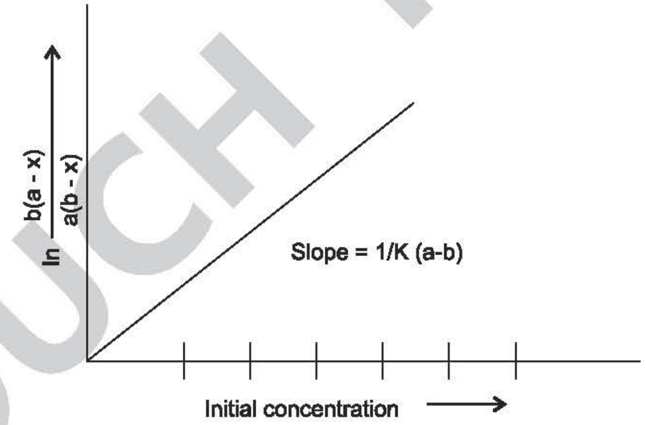


Fig. 9. $\ln\frac{b(a-x)}{a(b-x)}$ *Vs* initial concentration for second order reaction

Q.5. Describe the methods of determination of the order of reaction.

Ans.

Methods for Determination of Order of a Reaction

1. **Substitution method in integrated rate equation :** (Hit and Trial method) :
   - (i) The method can be used with various sets of a, x and t with integrated rate equations.
   - (ii) The value of k is determined and checked for all sets of a, x and t.
   - (iii) If the value of k is constant, the used equation gives the order of reaction.
   - (iv) If all the reactants are at the same molar concentration, the kinetic equations are :

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \qquad \text{(For first order reactions)}$$

$$k = \frac{1}{t}\left[\frac{1}{a} - \frac{1}{a-x}\right] \qquad \text{(For second order reactions)}$$

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] \qquad \text{(For third order reactions)}$$

2. **Half life method :** This method is employed only when the rate law involved only one concentration term.

$t_{1/2} \propto a^{1-n}; t_{1/2} = ka^{1-n}; \log t_{1/2} = \log k + (1-n)\log a$, a plotted graph of $\log t_{1/2}$ *Vs* $\log a$ gives a straight line with slope $(1-n)$, determining the slope we can find the order *n*. If half life at different concentration is given then.

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}}; (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}}; \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)[\log_{10} a_2 - \log_{10} a_1]$$

$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}$$

This relation can be used to determine order of reaction '*n*'.

Plots of half-lives *Vs* concentrations ($t_{1/2} \propto a^{1-n}$) :

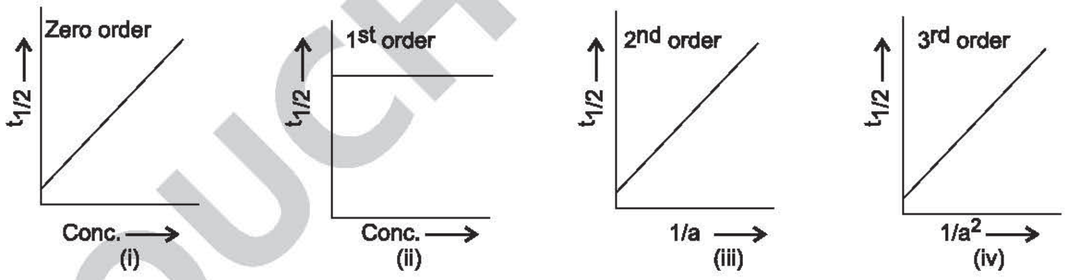


Fig. 10

3. **Graphical method :** A graphical method based on the respective rate laws, can also be used :
   - (i) If the plot of $\log(a-x)$ *Vs* t is a straight line, the reaction follows first order.
   - (ii) If the plot of $\frac{1}{(a-x)}$ *Vs* t is a straight line, the reaction follows second order.
   - (iii) If the plot of $\frac{1}{(a-x)^2}$ *Vs* t is a straight line, the reaction follows third order.
   - (iv) In general, for a reaction of *n*th order, a graph of $\frac{1}{(a-x)^{n-1}}$ *Vs* t must be a straight line.

Graphical determination of order of the reaction

Order	Equation	Straight line plot		Slope	Intercept on *Y*-axis
		Y-axis	*X*-axis		
Zero	$x = k_0 t$	x	t	k_0	0
First	$\log_{10}(a-x) = \frac{-k_1 t}{2.303} + \log_{10} a$	$\log_{10}(a-x)$	t	$\frac{-k}{2.303}$	$\log_{10} a$
Second	$(a-x)^{-1} = k_2 t + a^{-1}$	$(a-x)^{-1}$	t	k_2	a^{-1}
*n*th	$(a-x)^{1-n} = (n-1)\, k_n t + a^{1-n}$	$(a-x)^{1-n}$	t	$(n-1)k_n$	a^{1-n}

Plots from integrated rate equations

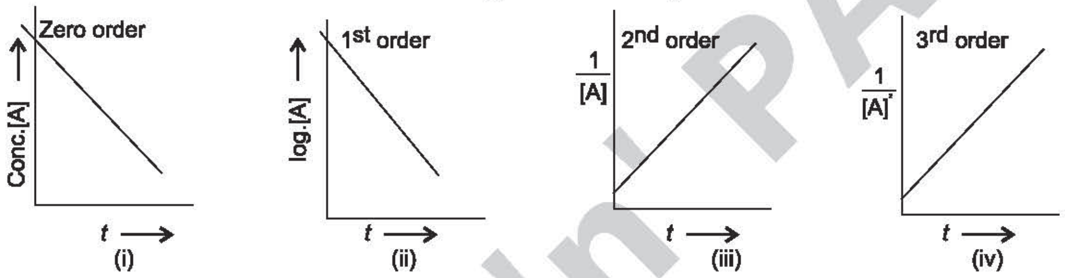


Fig. 11

Plots of rate vs concentrations [Rate = k (conc.)^n]

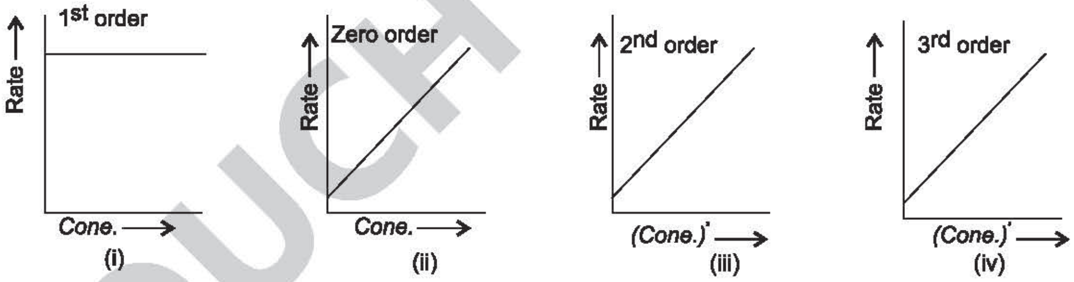


Fig. 12

4. **Van't Haff differential Method :** The rate of reaction varies as the *n*th power of the concentration. Where n is the order of the reaction. Thus for two different initial concentrations C_1 and C_2 equation, can be written in the form, $\frac{-dC_1}{dt} = kC_1^n$ and $\frac{-dC_2}{dt} = kC_2^n$.

Taking logarithms,
$$\log_{10}\left(\frac{-dC_1}{dt}\right) = \log_{10} k + n \log_{10} C_1 \quad \text{...(i)}$$

and
$$\log_{10}\left(\frac{-dC_2}{dt}\right) = \log_{10} k + n \log_{10} C_2 \quad \text{...(ii)}$$

Subtracting equation (ii) from (i),

$$n = \frac{\log_{10}\left(\frac{-dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2} \qquad \text{...(iii)}$$

$\frac{-dC_1}{dt}$ and $\frac{-dC_2}{dt}$ are determined from concentration *Vs* time graphs and the value of '*n*' can be determined.

5. **Ostwald's isolation method (Initial rate method) :** This method can be used irrespective of the number of reactants involved *e.g.*, consider the reaction, $n_1 A + n_2 B + n_3 C \rightarrow$ Products.

   This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (A, B, C). Now the concentration of one of the reactants is changed (say that of A) taking the concentrations of other reactants (B and C) same as before. The initial rate of the reaction is determined again. This gives the rate expression with respect to A and hence the order with respect to A. The experiment is repeated by changing the concentrations of B and taking the same concentrations of A and C and finally changing the concentration of C and taking the same concentration of A and B. These will give rate expressions with respect to B and C and hence the orders with respect to B and C respectively. Combing the different rate expressions, the overall rate expression and hence the overall order can be obtained.

   Suppose it is observed as follows :

   (i) Keeping the concentrations of B and C constant, if concentration of A is doubled, the rate of reaction becomes four times. This means, that Rate $\propto [A]^2$ *i.e.*, order with respect to A is 2.

   (ii) Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that, Rate $\propto [B]$ *i.e.*, order with respect to B is 1.

   (iii) Keeping the concentrations of A and B constant, if concentration of C is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of C *i.e.*, order with respect to C is zero. Hence the overall rate law expression will be, Rate $= k[A]^2\,[B][C]^0$

   $$\text{order of overall reaction} = 2 + 1 + 0 = 3$$

Q.6. (i) Describe the effect of temperature on rate of reaction.

(ii) What is Arrhevins equation? Describe activation energy.

Ans.

(i) Effect of Temperature on Rate of Reaction

The rate of reaction is very much affected by the temperature. Generally, the increment in the rate of almost all the reactions is observed on increasing temperature. On the contrary the rate of reactions decreases on decreasing temperature. This observation is observed in all the reactions, whether exothermic or endothermic. For example, in the decomposition of N_2O_5 the rate constant is found to be 7.87×10^{-7} sec^{-1} at 273 K which increases to 3.56×10^{-5} sec^{-1} at 298 K *i.e.*, on increasing temepratureby 25°C the rate of this reaction increases by 45 times.

According to a normal observation on increasing temperature by 10°C the rate of chemical reactions increases by 2 to 3 times.

$$\text{Temperature Coefficient} = \frac{\text{rate constant at } (T+10)^\circ\text{C}}{\text{rate constant (at } T^\circ\text{C)}} \approx 2 \text{ to } 3$$

According to collision theory the rate of a chronical reaction depends upon the collision frequency (z) and the fraction of effective collision (f). On increasing temperature the rate increment can also be explained on the basis of above two or any one factor.

1. **On increasing collision frequency :** On increasing temperature the average kinetic energy of reactant molecules increases which also increases the number of collisions per unit volume per second. The average kinetic energy of molecules is proportional to the absolute temperature. According to an observation, on increasing temperature from 300 K to 310 K the kinetic energy of molecules increases about 3%.

   It means that on increasing temperature the rate of reaction increases due to increase in collision frequency but it is not true because if it so then this increment of 10°C should have increased the rate by 3%. Actually the increase of 10°C temperature increases the rate of reaction by 2 to 3 times *viz.* 200 to 300%. So, the reason behind the increase in rate of reaction on increasing temperature is not only the increase in collision frequency.

2. **Increase in effective collision :** According to collision theory only some fraction of all the collisions is capable of doing chemical change which is known as effective collision. Effective collisions are collisions which produce energy equivalent to or more than the threshold energy. If the energy produced is less than the threshold energy then the collisions will not be able to make chemical changes. Hence these are known as non-effective collision.

   According to Maxwell Boltzmann, the energy distribution of molecules can be represented by statistics. All reactant molecules do not have equal energy. Molecules collide with each other due to this they transfer their energies to each other. If a curve is drawn between the energy of molecules and the fraction of molecules possessing energy it will be obtained as fig 13. This energy curve is known as Maxwell Boltzmann energy distribution curve.

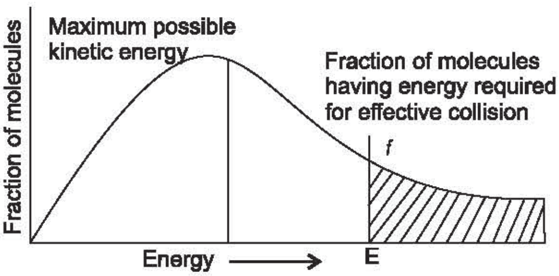


Fig. 13

From the curve it is clear that the fraction of molecules having low energy and high energy is comparatively low. Fraction of most of the molecules is having intermediate kinetic energy which is represented by the maxima of the curve and it is called maximum possible kinetic energy. In graph E is the minimum energy *i.e.*, threshold energy which is produced by the effective collisions and is capable of transforming reactants to products. The molecules having energy equal to or more than energy E are converted to the products which is a small fration of complete energy distribution.

It can be seen that lower the value of threshold energy E, higher will be the number of effective collision *i.e.*, higher will be the rate of reaction. On the countrary, on increasing the value of E, the number of effective collision will decrease which will decrease the rate of reaction.

Now we will focus upon the number of effective collisions on increasing temperature. Fig. 14. shows the distribution of the energy of molecules at T_1 and T_2 temperatures, where $T_2 = T_1 + 10°C$.

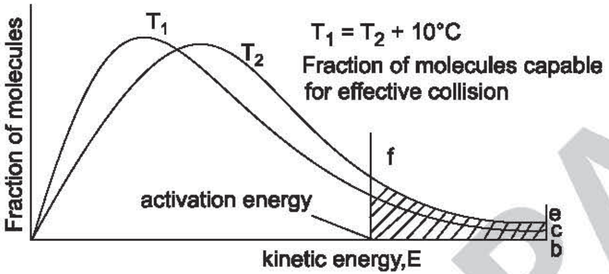


Fig. 14

From graph it is clear that on increasing temperature it has shifted towards right hand side and has become more flat. It means that on increasing temperature the energy distribution of molecules increases and the fraction of molecules having threshold energy becomes very high. At temperature T_1 the only fraction *abcd* does effective collision which becomes *abef* at temperature T_2. This fraction becomes almost double on increasing temperature $10°$. So it is clear that the main reason of increment in the rate of reaction on increasing temperature is the increment in the number of effective collisions.

(ii) The Arrhenius Equation

Temperature has a profound influence on the reaction velocity. In homogeneous thermal reactions, for every ten degree rise in temperature, the velocity of reaction is doubled or trebled. The ratio is called temperature coefficient.

$$\frac{K_{t+10}}{K_t} \approx 2 \text{ or } 3$$

Arrhenius (1889) showed that the velocity constant (K) of a chemical process increases exponentially with temperature for a large number of reactions. It was observed that the plot of log K against gives a linear relation.

Therefore, suggested empirically the relation as

$$\frac{d \ln K}{dT} = \frac{E}{RT^2}$$

or

$$K = Ae^{-E/RT} \quad (A = \text{constant})$$

A is called the frequency factor or pre exponential factor.

E is called the activation energy of the reaction.

These two quantities have definite values for any given reaction. By measuring the velocity constant K and $K^{/}$ at two temperatures T and $T^{/}$ respectively, we have

$$\log K = -\frac{E}{2.303\,R} \times \frac{1}{T} + \log A$$

$$\log K^{/} = -\frac{E}{2.303\,R} \times \frac{1}{T^{/}} + \log A$$

$$\log \frac{K}{K^{/}} = -\frac{E}{2.303\,R}\left[\frac{T^{/} - T}{TT^{/}}\right]$$

Hence the activation energy E is easily obtained.

Alternatively, a plot of log K against $\frac{1}{T}$ gives a straight line. The slope of such line gives the value of $\frac{E}{2.303\,R}$ from which E is evaluated. The intercept of the line would also enable one to find out the value of the frequency factor A.

Suppose K_1 and K_2 are the velocity constants in the two opposite directions of a reverisble process at temperature T.

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

$$\ln K_1 = -\frac{E}{RT} + \ln A_1 \text{ (constant)}$$

and $$\ln K_2 = -\frac{E_2}{RT} + \ln A_2 \text{ (constant)}$$

Subtracting, $$\ln \frac{K_1}{K_2} = \frac{(E_2 - E_1)}{RT} + \ln \frac{A_1}{A_2}$$

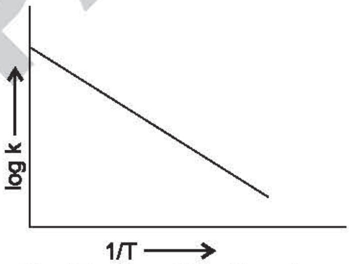


Fig. 15 : Plot of log *K* against 1/*T* for a reaction

But $$\frac{K_1}{K_2} = K, \text{ equilibrium constant of the reaction.}$$

Hence $$\ln K = \frac{E_2 - E_1}{RT} + \ln \frac{A_1}{A_2}$$

where E_1 and E_2 are the activation energies of the two opposite processes.

Hence $$\frac{d \ln K}{dT} = -\frac{(E_2 - E_1)}{RT^2} = \frac{E_1 - E_2}{RT^2}$$

But from Vant Hoff equation $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$

where ΔH is the heat change of the chemical process. Comparing the two expressions we get,

$$\Delta H = E_1 - E_2$$

Activation energy of a reaction : its significance : The average energy of the reactant is represented by E_A and that of the resultant by E_B. But if E_A is greater than E_B the reactant A will not be straight way transformed to the product B. There is a minimum energy level for the reaction denoted by Ex to which the reactant molecule must be raised in order to enable it to undergo the chemical change.

The excess or additional energy $(E_X - E_A)$ which the reactant must acquire in order to undergo transformation is the activation energy E_1.

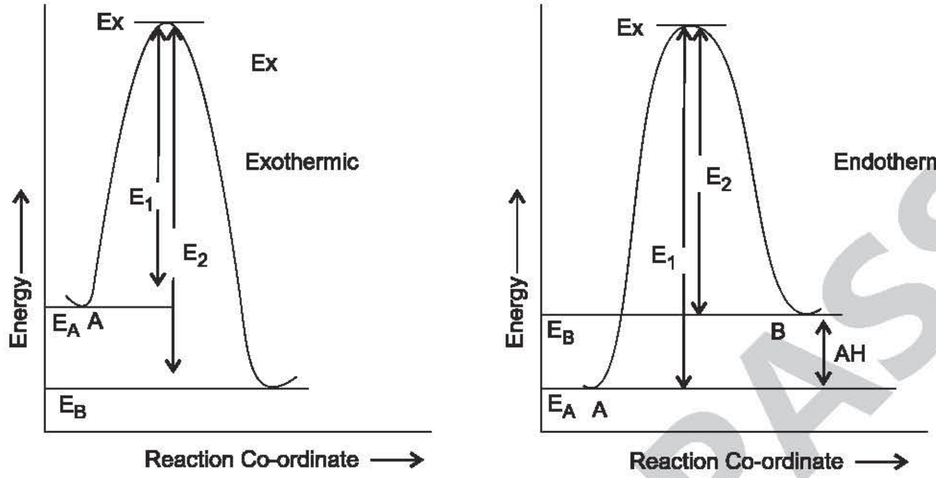


Fig. 16 : Potential energy profile of exothermic and endothermic reaction

Molecule, having energy E_X or above are said to be in activated state and such molecules only are fit for chemical reaction.

If $E_2 > E_1$, the reaction is evidently exothermic, where as if $E_2 < E_1$, the reaction is endothermic.

Q.7. Describe simple collision theory and transition state theory.

Ans.

Collision Theory

The collision theory explains the mechanism of bimolecular reactions, but with unimolecular reactions the theory apparently fails. In the unimolecular reactions which are also of the first order, only one molecule takes part in the reaction.

According to Lindemann hypothesis the molecules acquire activation energy through collisions, but the activated molecules decompose only after some time has elapsed after the collision. That is, there is a time lag between the moment of activation and the moment of decomposition. When this time lag is relatively large, there is every possibility for most of the activated molecules being deactivated by subsequent collisions to ordinary molecules. As a result, the rate of decomposition will not be proportional to all the activated molecules but only to a fraction which survives the time lag. The activated molecules therefore disappears through two parallel processes, namely through deactivation and through decomposition.

(i) $A + A \xrightarrow{K_1} A + A^*$ Rate of activation $\frac{dC_A^*}{dt} = K_1 C_A^2$

(ii) $A^* + A \xrightarrow{K_2} 2A$ Rate of deactivation $-\frac{dC_A^*}{dt} = K_2 C_A C_A^*$

(iii) $A^* \xrightarrow{K_3} B + C$ (Products) Rate of decomposition $-\frac{dC_A^*}{dt} = K_3 C_A^*$

where A represents ordinary and A^* activated molecules.

The rate of reaction of A is the rate at which products are formed

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = K_3 C_A^*$$

Now, activated molecules are short lived and have a small concentration at any time during the process. So from the steady state principle, the rate of formation of A^* molecules and the rate of their disappearance would be the same

$$K_1C_A^2 = K_2C_AC_A^* + K_3C_A^*$$

$$C_A^* = \frac{K_1C_A^2}{K_2C_A + K_3}$$

∴ Rate of reaction, $$-\frac{dC_A}{dt} = K_3C_A^* = \frac{K_1K_3C_A^2}{(K_2C_A + K_3)}$$

Case 1 : When rate of deactivation is very large compared with that of decomposition *i.e.*, when $K_2C_A >> K_3$

$$-\frac{dC_A}{dt} = \frac{K_1K_3}{K_2}C_A$$

$$-\frac{dC_A}{dt} = K^/C_A$$

which is the expression for first order kinetics.

Case 2 : When concentration C_A is lowered considerably, the chances of deactivation by collision decrease largely, then $K_3 >> K_2C_A$, hence we have,

$$-\frac{dC_A}{dt} = K_1C_A^2$$

Thus at low concentration the process would follow second order kinetics.

Transition State Theory : According to this theory, the two reactants say, *AB* and *C* first form a transition complex *A—B—C* which then decomposes into *A* and *BC*.

The basic idea is that, we must some how force *C* to come so close to *B* that *B* becomes undecided as to which atoms it now belongs to. This state of indecision as to *B*, being simultaneously attached both to *A* and *C*, though some how loosely than before, is the transition state, also called the activated complex. The energy necessary to push *C* to approach *B* to form this transition state or activated complex is the energy of activation. The observed rate of reaction would be equal to the net rate of formation of the activated complex.

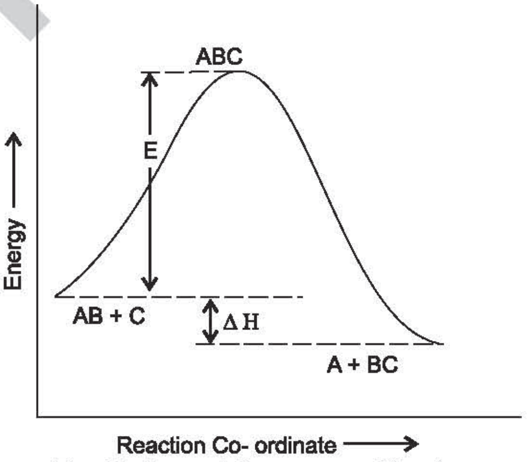


Fig. 17 : Potential energy profile of an exothermic reaction

UNIT-II

Chemical Equilibrium

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Which properties do remain constant in the following equilibrium?

(i) Solid $\rightleftharpoons$ Liquid (ii) Liquid $\rightleftharpoons$ Gas

Ans. (i) M.P. (ii) vapour pressure

Q.2. Can Liquid $\rightleftharpoons$ Gas equilibrium be attained in an open vessel?

Ans. No

Q.3. A gas is in equilibrium with water at a certain temperature and pressure. What will happen if :

(i) temperature is increased,

(ii) pressure of the gas is increased?

Ans. (i) Solubility of gas in water will decrease. (ii) Solubility of gas in water will increase.

Q.4. Can a catalyst affect the state of chemical equilibrium?

Ans. No

Q.5. Sort out the homogeneous and heterogeneous equilibria from the following :

(i) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(ii) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Ans. (i) Heterogeneous, (ii) Homogeneous

Q.6. Write the equilibrium constant expression for the following reactions :

(i) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(ii) $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

(iii) $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Ans. (i) $K = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$, (ii) $K = [Ba^{2+}][SO_4^{2-}]$, (iii) $K = \dfrac{[H_3O^+][Cl^-]}{[HCl]}$

Q.7. State the unit of K_p and K_c for the reaction :

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Ans. $mol^{-1}L$, atm^{-1}

Q.8. The value of equilibrium constant for the reaction

$$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$$

is 5.0×10^8. In which direction is the reaction expected to proceed to a greater extent?

Ans. forward direction

Q.9. What will be the effect of increasing temperature on an exothermic reaction?

Ans. Backward reaction will be favoured

Q.10. Can equilibrium be achieved between water and its vapour in an open vessel.

Ans. No

Q.11. Give two examples of irreversible reactions.

Ans. (i) $CaCO_3 \longrightarrow CaO + CO_2$

(ii) $2Na + 2H_2O \longrightarrow 2NaOH + H_2$

Q.12. Give two examples of reversible reactions.

Ans. (i) $N_2O_4 \rightleftharpoons 2NO_2$

(ii) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Q.13. What is equilibrium constant?

Ans. Equilibrium constant k is the ratio of product of the active masses of the products to that of the reactants in equilibrium with each active mass term raised to the power equal to the stoichiometric coefficient of the substance in the balanced chemical equation.

Q.14. Write the relation between k_p and k_c.

Ans. $k_p = k_c\,(RT)^{4n}$

Q.15. Discuss the effect of increase of pressure on the following reactions :

(i) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Ans. (i) No effect, (ii) Backward reaction is favoured

Q.16. In which direction is equilibrium expected to shift on increasing temperature in the following reactions?

(i) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g); \Delta H = +212.8$ **kcal**

(ii) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \Delta H = -42$ **kcal**

Ans. (i) Forward direction, (ii) Backward direction.

Q.17. Discuss the conditions for obtaining the maximum yield in the following reactions.

(i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H = -22$ **kcal.**

(ii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \Delta H = 43.2$ **kcal.**

Ans. (i) Low temperature, high pressure; (ii) High temperature

Q.18. For a general reaction

$$2A + B \rightleftharpoons C + 3D; \Delta H = +x \text{ kcal.}$$

what will be the effect of (i) decrease in volume, (ii) increase in temperature, (iii) increase of pressure at equilibrium?

Ans. (i) Higher yield of products, (ii) Higher yield of products, (iii) Backward reaction favoured.

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What do you mean by static and dynamic equilibrium.

Ans.

Static and Dynamic Equilibrium

The state equilibrium can be observed in physical and chemical systems. Also, equilibrium can be static or dynamic in nature. A book lying on the table is an example of static equilibrium. The forces of action and reaction cancel each other and no change takes place. thus it is a case of static equilibrium. On the other hand, when an escalator is coming down and passenger is going up at the same speed it is a case of dynamic equilibrium. Here, because both are moving in opposite directions and at the same speed, no net change takes place. The equilibrium established in the above examples are in physical systems.

Q.2. Write a short note on reversible reactions.

Ans.

Reversible Reactions

Not all chemical reactions proceed to completion. In most reactions two or more substances react to form products which themselves react to give back the original substances. Thus A and B may react to form C and D which react together to reform A and B.

$$A + B \longrightarrow C + D \text{ (Forward reaction)}$$

$$A + B \longleftarrow C + D \text{ (Reverse reaction)}$$

A reaction which can go in the forward and backward direction simultaneously is called a Reversible reaction. Such a reaction is represented by writing a pair of arrows between the reactants and products.

$$A + B \rightleftharpoons C + D$$

The arrow pointing right indicates the forward reaction, while that pointing left shows the backward reaction.

Some Examples of reversible reactions :

A few common examples of reversible reactions are listed below :

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$PCL_5 \rightleftharpoons PCl_3 + Cl_2$$

Q.3. What are irreversible reactions?

Ans.

Irreversible Reactions

Most of the reactions occur only in one direction. They are called irreversible reactions. For example when carbon is burnt in air to form carbon dioxide the reaction goes only in one direction *i.e.*, in the direction of formation of carbon dioxide.

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

Strictly speaking all reactions are considered to be reversible. But the rate of reaction in one particular direction is extremely small compared to the other. Thus the reaction proceeds practically in one direction to near completion, leaving a negligibly small amount of reactant at the end.

When hydrochloric acid is mixed with sodium hydroxide, a base, in equimolar quantities, a neutralisation reaction takes place; with the formation of salt and water.

$$HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$$

This reaction proceeds to completion in the forward direction. Similarly when a solution of silver nitrate is added to a solution of sodium chloride silver chloride is precipitated immediately.

$$NaCl(aq) + AgNO_3\,(aq) \text{—} AgCl\,(s) + NaNO_3\,(aq)$$

Q.4. Write a short note on chemical equilibrium.

Ans.

Chemical Equilibrium

Let us consider the reaction :

$$A + B \rightleftharpoons C + D$$

If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D increase continuously. As a result the rate of forward reaction also decrease and rate of backward reaction increases. Ultimately, the rate of two opposing reactions equals and the system attains a state of equilibrium. Thus "the state of reversible reaction in which the concentrations of the reactants and products do not change is called chemical equilibrium".

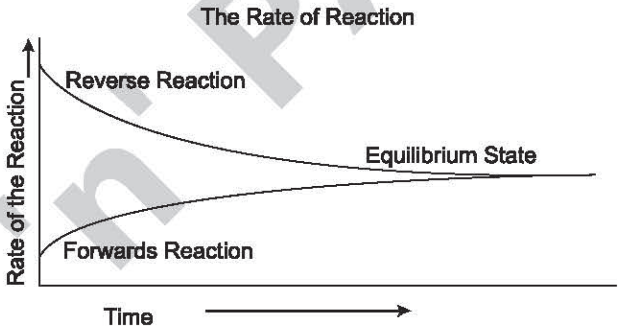


Fig. 1 : At equilibrium the Forward reaction rate equals the Reverse reaction rate

Characteristics of chemical Equilibrium : Some of the important characteristics of chemical equilibrium are follows :

1. At equilibrium, the concentration of each of the reactants and products becomes constant.
2. At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence the equilibrium is dynamic in nature.
3. A chemical equilibrium can be established only if none of the products is allowed to escape out.
4. Chemical equilibrium can be attained from either direction *i.e.*, from the direction of reactants as well as from the direction of the products.
5. A catalyst does not alter the state of equilibrium.

Q.5. What are the characteristics of equilibrium state?

Ans.

Characteristics of Equilibrium State

The state of chemical equilibrium is reached in a reversible reaction when :

1. The temperature of the system attains a constant value.
2. The pressure of the system attains a constant value.
3. The concentrations of all the reactants and products attain constant values.

The state of equilibrium has following characteristics properties :

1. **Chemical Equilibrium is dynamic in nature :** The chemical equilibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no "net" change occurring in the system.
2. **Equilibrium can be attained from either side :** The same state of equilibrium (characterized by its equilibrium constant which is discussed later can be reached whether the reaction is started from the reactants or products side. For eample, the same equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

   is established whether we start the reaction with N_2O_4 or NO_2.
3. **Equilibrium can be attained only in a closed system :** Equilibrium can be attained only if no substance among, reactants or products, is allowed to escape *i.e.*, the system is a closed one. Any system consisting of gaseous phase or volatile liquids must be kept in a closed container, *e.g.*,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

   A system consisting of only non-volatile liquid and solid phases can be kept even in an open container because such substances have no tendency to escape, *e.g.*,

$$FeCl_3(aq) + 3NH_4SCN(aq) \rightleftharpoons Fe(SCN)_3(s) + 3NH_4Cl(aq)$$

4. **A catalyst can not change the equilibrium state :** Addition of a catalyst speeds up the forward and reverse reactions by same extent and help in attaining the equilibrium faster. However, the equilibrium concentrations of reactants and products are not affected in any manner.

Q.6. What do you mean by homogeneous and heterogeneous systems?

Ans.

Homogeneous and Heterogeneous Systems

Homogeneous system is one which has one phase. It has the same chemical composition and uniform properties throughout. It is formed by particles of molecular size only. Pure solids, liquids, gases and solutions are the examples of homogeneous systems.

A system consisting of only one phase is called a homogeneous system.

Heterogeneous system, on the other hand has at least two phases—a mixture of solids or immiscible liquids constitutes a heterogeneous system.

Any system consisting of two or more phases is called heterogeneous system.

Q.7. Discuss in brief homogeneous and heterogeneous equilibrium systems with examples.

Ans.

Homogeneous and Heterogeneous Equilibrium System

Equilibrium can be established in either type of systems. Since all physical equilibria involve at least two phases, therefore these are all examples of heterogeneous equilibrium. But chemical equilibrium can be homogeneous or heterogeneous in nature. It is homogeneous if both the reactants and products are present only in one phase gas or liquid and heterogeneous if present in more than one phase. In the given sections we shall study such systems.

1. Homogeneous Chemical Equilibrium System

1. **Gas : Phase homogeneous systems :** Such systems contain only gaseous reactants and products. Since all gaseous mixtures are homogeneous in nature they constitute only one phase. Following are examples of this type of equilibrium :
   (i) $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$
   (ii) $2N_2O_5(g) \rightleftharpoons 4NO_2(g)+O_2(g)$
2. **Liquid : Phase homogeneous systems :** These are the systems in which both the reactants and products are present in only one liquid phase (as a solution) for example :
   (i) $CH_3COOH(l)+C_2H_5OH(l) \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5(l)+H_2O(l)$
   (ii) $KCN(aq)+H_2O\,(l) \rightleftharpoons HCN\,(aq)+KOH\,(aq)$

2. Heterogeneous Chemical Equilibrium System

The system in which reactants and products are present in more than one phase belong to this type. For example :

1. $Fe\,(s)+4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s)+4H_2\,(g)$
2. $CaCO_3\,(s) \rightleftharpoons CaO\,(s)+CO_2\,(g)$

Q.8. The vapour pressure of water 95°C and 100°C are 634 and 760 mm, respectively. Calculate the latent heat of evaporation of water per gram between 95°C and 100°C.

Ans.

$$\log \frac{p_2}{p_1} = \frac{\Delta H_V}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Where p_1 and p_2 are vapour pressure at temperature T_1 and T_2 respectively and ΔH_V is the latent heat of evaporation/mole. It is given that

$$P_1 = 634 \text{ mm}$$
$$P_2 = 760 \text{ mm}$$
$$T_1 = 95+273 = 368° \text{ K}, \; T_2 = 100+273 = 373° \text{ K}$$

So,
$$\log \frac{760}{634} = \frac{\Delta H_V}{2.303 \times 1.987}\left[\frac{373-368}{368 \times 373}\right]$$

or
$$H_V = 9886 \frac{\text{cal}}{\text{mole}} = \frac{9886}{18} = 549.4 \frac{\text{cal}}{\text{g}}.$$

Q.9. At what height must the barometer stand in order that water may boil at 99°C? Given that the latent heat of vaporization of water per gram is 536 cal.

Ans. As known, the integrated form of Clausius-Clapeyron equation is,

$$\log \frac{p_2}{p_1} = \frac{\Delta H_V}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$P_1 = 76$ cm mercury, $P_2 = ?$, $T_1 = 100+273 = 373$ K, $T_2 = 99+273 = 372$ K

$$\Delta H_V = 536 \text{ cal/g} = 536 \times 18 \text{ cal/mole}$$

$$\log\frac{p_2}{76}=\frac{535\times18}{2.303\times1.987}\left[\frac{372-373}{372\times373}\right]=\left[-\frac{536\times18\times1}{2.303\times1.987\times372\times373}\right]$$

$$\log p_2-\log 76=-\frac{536\times18\times1}{2.303\times1.987\times372\times373}$$

or

$$\log p_2=\log 76-\frac{536\times18\times1}{2.303\times1.987\times372\times373}$$

$$=1.8806-0.0159=1.8659$$

taking antilog we get $p_2=73.43$ cm of mercury.

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. (i) What is law of mass action?

(ii) Describe the law of chemical equilibrium and equilibrium constant.

Ans.

(i) Law of Mass Action

Gulberg and Waage, the two Norwegian chemists, in **1864** put forward a law concerning the dependence of rate of reaction on the concentration of the reactants. This law is known as Law of Mass Action. It states as follows : The rate of chemical reaction is proportional to the active masses of the reactants.

The term active mass used in the above statement implies activity which, for the sake of simplicity, may be taken as equal to molar concentration.

Consider the following reversible reaction, taking place at constant temperature :

$$A+B\rightleftharpoons C+D$$

According to the law of mass action, the rate (r_1) at which A and B react is given by the equation

$$r_1\propto[A][B]$$

$$r_1=k_1[A][B] \qquad \text{...(i)}$$

Where k_1 is the proportionality constant, called rate constant of the reaction and the square brackets indicate molar concentrations. The rate of backward reaction (r_2) is given by the equation.

$$r_1=k_2[C][D] \qquad \text{...(ii)}$$

Where k_2 is the rate constant of reverse reaction.

Thus ultimately, a dynamic equilibrium is attained when the rate of forward reaction becomes equal to that of the reverse reaction, *i.e.*, $r_1=r_2$.

(ii) Law of Chemical Equilibrium and Equilibrium Constant

consider the following reversible reaction :

$$aB+bB\rightleftharpoons cC+dD$$

Where a, b, c and d are numerical quotients of the substance, A, B, C and D respectively.

According to law of mass action,

Rate of forward reaction, $r_1=k_1[A]^a[B]^b$

Rate of backward reaction, $r_2=k_2[C]^c[D]^d$

Since at equilibrium, $r_1=r_2$, it follows that

$$k_1\,[A]^a\,[B]^b = k_2\,[C]^c\,[D]^d$$

or
$$\frac{k_1}{k_2} = k_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad \text{...(i)}$$

k_c is known as equilibrium constant and has a fixed value for a certain reaction at a given temperature and pressure and is independent of the amounts of reactants and products. However, its value depends on the temperature and types of reactions.

In a general reaction reprinted by the equation
$$aA + bB + cC + \ldots \rightleftharpoons lL + mM + nN + \ldots$$

The equilibrium constant is given by
$$k_c = \frac{[L]^l\,[M]^m\,[N]^n \ldots}{[A]^a\,[B]^b\,[C]^c \ldots} \qquad \text{...(ii)}$$

For gaseous reactions, it is more convenient to use partial pressures instead of concentrations.

The equilibrium constant in that case is represented by K_p.

Thus for a general gaseous reaction
$$aA + bB + cC + \ldots \rightleftharpoons lL + mM + nN + \ldots$$
$$K_p = \frac{[P_L]^l \times [P_M]^m \ldots}{[P_A]^a \times [P_B]^b \ldots} \qquad \text{...(iii)}$$

Where P_L and P_M etc. stand for partial pressures of the products and P_A, P_B, etc for the partial pressures of the reactants.

Q.2. (i) Describe the relationship between k_P and k_C.

(ii) Write a note on free energy and chemical equilibrium.

Ans.

(i) Relationship between K_P and K_C

For a general reaction,
$$aB + bB \rightleftharpoons cC + dD$$

The equilibrium constant in terms of concentrations (moles/liter) is
$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad \text{...(i)}$$

If the reactants and products are gaseous, then the concentration terms may be replaced by partial pressure. The equilibrium constant K_p written as,
$$K_p = \frac{p_C^c\,p_D^d}{p_A^a\,p_B^b} \qquad \text{...(ii)}$$

For an ideal gas, $pV = nRT$ or $p = \frac{n}{V}RT = CRT.$

Where C is the molar concentration. For different gases A, B, C, D we may write
$$P_A = C_A RT,\ p_B = C_B RT,\ p_C = C_C RT,\ p_D = C_D RT$$

Putting these values in equation (ii), we get
$$K_p = \frac{(C_C RT)^c\,(C_D RT)^d}{(C_A RT)^a\,(C_B RT)^b}$$

or
$$K_p = \frac{C_C^c\, C_D^d}{C_A^a\, C_B^b}(RT)^{(c+d)-(a+b)}$$

Where
$$K_p = K_c\,(RT)^{\Delta n} \qquad \text{...(iii)}$$

$$\Delta n = (c+d)-(a+b) = [\text{number of moles of products}] - [\text{number of moles of reactants}]$$

(ii) The Free Energy and Chemical Equilibrium

Gibbs free energy or thermodynamic potential provides true measure of chemical affinity under conditions of constant temperature and pressure. The free energy change during a chemical reaction can be defined as follows :

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

At constant temperature and pressure, the system will move in the direction of decreasing free energy. Suppose a chemical reaction occurs, the reactants will react until a state of minimum free energy is attained.

Once the system reaches the equilibrium state, it can neigher go in the direction of G_R nor in the direction of G_P, because shift of the system from equilibrium state in any direction leads to increase in the free energy.

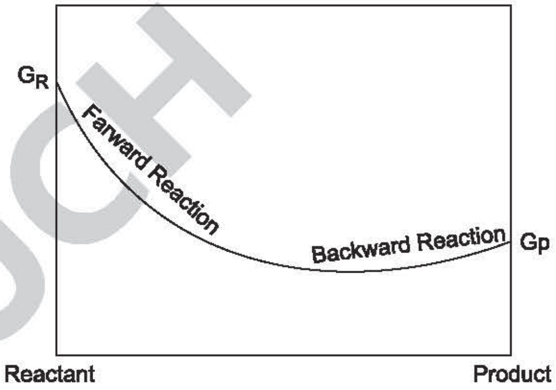


Fig. 2 : The free energy change of a reaction

So, it can be said that the equilibrium state is the state of minimum Gibbs free energy and the tendency of the reaction is proceed at constant T and P is measured by $-\Delta G$. For this reason $-\Delta G$ has often been called the driving force of a reaction.

Now, since $\Delta G = \Delta H - T\Delta S$

Here (ΔH and ΔS are change in enthalpy and entropy).

Driving force of process is $= -\Delta G = -\Delta H + T\Delta S$. For large driving force it is necessary to have ΔH as negative as possible and ΔS as positive as possible.

It is common in practice to use standard free energy data to describe the feasibility of a chemical reaction.

The standard free energy change of a process can be defined as follows :

"The change in free energy when the reactants and products of a reaction are in their standard state (*i.e.*, 298 K temperature, 1 atm pressure) is known as the standard free energy (ΔG°) of the process."

Thus, $$\Delta G^\circ = \Sigma G^\circ_{\text{Products}} - \Sigma G^\circ_{\text{Reactants}}$$
$$= \Delta H^\circ - T\Delta S \qquad \text{(at constant } T\text{)}$$

The values of ΔG° can be calculated from the known data of ΔH° and ΔS°.

If ΔG° (ΔG at constant temperature) is negative, the reaction is feasible; if it is zero, the reaction is in the state of equilibrium and if it is positive, the reaction is not feasible.

Q.3. Derive law of mass action thermodynamically.

Ans.

Thermodynamic Derivation of the Law of Chemical Equilibrium

Let us consider a general reaction,

$$aA + bB + \ldots \rightleftharpoons cC + dD + \ldots$$

The chemical potential of a substance in a mixture is related to its activity by the expression

$$\mu = \mu^\circ + RT \ln a \qquad \text{...(i)}$$

Where μ° is the chemical potential of pure substance in standard state of unit activity, R is the gas constant and T is the absolute temperature.

For a mole of the substance A we can write using the equation (i)

$$a\mu_A = a\,(\mu^0 + RT \ln a_A)$$

And similarly
$$b\mu_S = b\,(\mu^0 + RT \ln a_B)$$
$$c\mu_C = c\,(\mu^0 + RT \ln a_C)$$
$$d\mu_D = (\mu^0 + RT \ln a_D)$$

The change in free energy for the reaction is given by

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

On substitution we get

$$(c\mu_c + d\mu_D + \ldots) - (a\mu_A + b\mu_B) = \ldots$$
$$= (c\mu_c + d\mu_D + \ldots) - (a\mu_A + b\mu_B + \ldots)$$
$$= c\,[\mu_C^0 + RT \ln a_C) + d\,[\mu_D^0 + C] - [a(\mu_a^0 + RT \ln a_A)$$
$$+ b\,[\mu_{\text{B}}^0 + RT \ln a_B]$$
$$= [\{c\mu_C^0 + d\mu_D^0 + \ldots\} - \{a\mu_A^0 + \mu_B^0 + \ldots\}] + RT \ln \frac{a_C^c + a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots} \qquad \text{...(ii)}$$

Where ΔG^0 is the difference in free energy of the reaction when all reactants and products are in their standard state. it is given by

$$\Delta G^\circ = \{c\mu_C^0 + d\mu_D^0 + \ldots\} - \{a\mu_A^0 + \mu_B^0 + \ldots\}$$

In equation (ii) the factor A is given by

$$\frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots}$$

Stands for the reaction quotient of activities of the product and reactants. It may be denoted by J. The equation (ii) becomes,

$$\Delta G = \Delta G° + RT \ln J \qquad \text{...(iii)}$$

The equation (iii) is called van't Hoff reaction isotherm.

For the reaction at equilibrium

$$\Delta G = 0$$

Therefore, $$\Delta G° = -RT \ln J$$

or $$\Delta G° = -RT \ln \frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots}$$

As $\Delta G°$ is the free energy of the reaction in the standard state and is constant at given temperature.

Also, the gas constant R and T are constant, the factor

$$\frac{a_C^c \times a_D^d \times ..}{a_A^a \times a_B^b \times \ldots} \text{ is a constant } i.e.,$$

$$\frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots} = a \text{ constant} = K$$

From equation (iii) we have

$$\Delta G° = -RT \ln K \qquad \text{...(iv)}$$

or $$c = -2.303\, RT \log K \qquad \text{...(v)}$$

The equation (iv) is also called **van't Hoff Isotherm.** It may be used to calculate the change in free energy of a reaction in the standard ($\Delta G°$) from the equilibrium constant and **vice-versa**.

The sign of $\Delta G°$ indicates whether the forward or reverse reaction is spontaneous. Considering the equation (iv), we can have three possibilties depending on the sign of $\Delta G°$ for the reaction.

1. If $\Delta G°$ is negative, log K must be positive and the reaction proceeds spontaneously in the forward reaction.
2. If $\Delta G°$ is positive, log K must be negative and K is less than one. The reverse reaction is then spontaneous.
3. If $\Delta G° = 0$, log $K = 0$ and $K = 1$. The reaction is at equilibrium.

Q.4. State and explain Le-chatelier's principle. Explain the effect of pressure and temperature on equilibrium on the basis of this principle.

Ans.

Le Chatelier's Principle

It states that when a system in equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor.

The principle can be applied to various situations.

Change in Concentration

Consider the state of equilibrium for the formation of ammonia from nitrogen and hydrogen.

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H=-92.4 \text{ kJ/mol}$$

The concentration of nitrogen, hydrogen and ammonia become constant at the point of equilibrium. Now if any amount of reactants or ammonia is added or removed their concentration will change and the equilibrium will get disturbed.

1. **Increase concentration of reactant :** When the concentration of either nitrogen or hydrogen is increased; a net forward reaction will take place which consumes the added reactant.
2. **Increase in the concentration of any product :** If the concentration of product ammonia is increased, a net backward reaction would take place to utilise the added ammonia.

Change in Pressure

Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or hetrogeneons system.

Le Chatelier's principle for systems involving gases can be studied as follows :

1. When the number of moles of products is more than the total number of moles of reactants as in the following system :

   $$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

   Increase in total pressure keeping the temperature constant, will cause a decrease in volume. This means that the number of moles per unit volume will increase. A net change will take place in the equilibrium in the direction where the number of moles decreases *i.e.*, backward direction.
2. When the number of moles of products is less than reactants. As in the following case

   $$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

   According to Le Chatelier's principle increase in total pressure will bring a net change to the equilibrium in the direction where the total number of moles is decreasing *i.e.*, to the product side as $\Delta n_g = 2$. Decrease in total pressure will bring the net change to equilibrium in the direction where the total number of moles is increasing *i.e.*, backward direction.
3. When there is no change in the total number of moles of reactant and product as in the following state of equilibrium.

   $$H_2(g)+I_2(g) \rightleftharpoons 2HI$$

There is no net change in equilibrium state when pressure is changed.

Change of Temperature

According to Le Chatelier principle when the temperature is changed (increased or decreased) the equilibrium system reacts to nullify the change in heat content. However, the net change in equilibrium is directed by the exothermic or endothermic nature of reaction.

1. **Exothermic equilibrium :** For the following system of equilibrium of exothermic nature :

   $$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H=-92.4 \text{ kJ/mol}$$

according to Le Chatelier principle increase in temperature brings a net change in the equilibrium state in that direction where this extra heat is consumed. The net change is in the backward direction and some ammonia will decompose producing nitrogen and hydrogen. similarly if the temperature is decreased the equilibrium shifts to the forward direction.

2. **Endohermic equilibrium :**

$$N_2(g)+O_2(g) \rightleftharpoons 2NO(g); \quad \Delta H = +180.7 \text{ kJ/mol}^{-1}$$

If the temperature is increased the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the forward direction. If the temperature in decreased it will bring a 'net' change to equilibrium in the backward direction *i.e.*, direction in which it is exothermic.

Addition of Catalyst : It does not affect the equilibrium. However it helps to achieve the equilibrium faster.

Applications of Le Chatelier's Principle

It can be applied to physical as well as chemical equilibria

(A) Physical Equilibria

1. **Melting of Ice :**

$$\text{Ice} \rightleftharpoons \text{Water}; \qquad \Delta H = +6 \text{ kJ/mol}^{-1}$$

The change of ice of water is endothermic process. According to Le Chatelier principle if the temperature is increased the net change will take place in the forward direction some ice will melt into water.

When the pressure is increased on the equilibrium system, then the volume should decrease; according to **Le Chatelier principle** the net change in equilibrium takes place in the forward direction and ice melts. Therefore, ice melts on increasing the pressure.

2. **Vaporization of Water :**

$$\text{Water (l)} \rightleftharpoons \text{Water vapour}; \qquad \Delta H = +\text{ve}$$

This process occurs with a large increase in volume since $\Delta n_g = 1 - 0 = +1$, and it occurs with absorption of heat.

Increasing the temperature results in more vapour formation (endothermic process). Since $\Delta n_g = +1$, increase in pressure results in a net change in equilibrium in the backward direction as the volume of water vapours is more than that of liquid water for a given mass of water.

3. **Solubility Equilibrium :** The equilibrium is

$$\text{Solute } (s) \rightleftharpoons \text{Solute (solution)}$$

The process of dissolution can be endothermic or exothermic. In case of solutes like KCl, KNO_3 and NH_4Cl, ΔH is positive (endothermic) and more solute will dissolve on heating. Thus, the solubility increases with rise in temperature. In case of solutes like KOH and NaOH the ΔH is negative (exothermic) and their solubility decreases on heating.

(B) Chemical Equilibria

1. **Favourable Conditions for Synthesis of Ammonia :** This reaction is of great industrial importance. During the synthesis of ammonia such conditions are maintained which favour the 'net' forward reaction namely low temperature and high pressure. Addition of catalyst makes the reaction occur fast. Besides, nitrogen and hydrogen gases are continuously fed into the reaction chamber and ammonia is continuously removed. All this keeps the system under stress and equilibrium is never permitted to be attained, so that the synthesis of ammonia continues to occur.

   In industry the reaction is carried out at 450°C and 200 atm pressure in the presence of finely divided iron (catalyst) and molybdenum (promotor).

2. **Formation of SO_3 :** The reaction

   $$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g);\quad \Delta H = -\text{ve}$$

   is exothermic and $\Delta n_g = 2-3 = -1$. Formation of SO_3 will be favoured by high pressure and low temperature in the presence of a catalyst.

3. **Formation of NO :** The reaction

   $$N_2(g)+O_2(g) \rightleftharpoons 2NO\,(g);\qquad \Delta H = +\text{ve}$$

   is endothermic and $\Delta n_g = 2-2 = 0$. The reaction is not affected by pressure changes and is favoured at high temperature. Presence of a suitable catalyst would be helpful.

Q.5. Describe the following on the basis of thermodynamics :

(i) Van't Hoff isotherm.

(ii) Van't Hoff isochore.

Ans.

(i) Van't Hoff Isotherm or Maximum Work Obtained from Gaseous Reactions

Consider the following reaction

$$aA + bB + \ldots \rightleftharpoons lL + mM + \ldots$$

Taking place under any conditions of temperature, pressure and composition. The free energy change of the reaction is given by the expression

$$\Delta G = (G)_{\text{products}} - (G)_{\text{reactants}} \qquad \ldots\text{(i)}$$

$$= (l\mu_L + m\mu_M + \ldots) - (a\mu_A + b\mu_B + \ldots)$$

Where $\mu_A, \mu_B, \mu_L, \mu_M$, etc represents chemical potentials of the species concerned.

Let us suppose the various reactants and products are in gaseous state. Chemical potential of a gaseous substance in any state is given by the equation

$$\mu_{t(p)} = \mu^0_{t(p)} + RT \ln p_i \qquad \ldots\text{(ii)}$$

Where $\mu^0_{t(p)}$ is the chemical potential of gaseous component i, in the standard state (partial pressure = 1 atm) and $\mu_{t(p)}$ is the chemical potential of the gaseous component i in any state of partial pressure p_i.

Substituting the values of chemical potentials of various species at their partial pressures from eq. (ii) in equation (i)

$$\Delta G = [l\,(\mu^0_{L(p)} + RT \ln p_L) + m\,(\mu^0_{M(p)} + RT \ln p_M) + \ldots]$$

$$-[a\,(\mu^0_{A(p)} + RT \ln p_A) + b\,(\mu^0_{B(p)} + RT \ln p_B) + \ldots] \quad \ldots\text{(iii)}$$

Rearranging we have
$$\Delta G = [(l\mu^0_{L(p)} + m\mu^0_{M(p)} + \ldots) - (a\mu^0_{A(p)} + b\mu^0_{B(p)} + \ldots)]$$

$$+ RT \ln \frac{(P_L)^l\,(P_M)^m \ldots}{(P_A)^a\,(P_B)^b \ldots} \quad \ldots\text{(iv)}$$

The first expression on the right hand side, evidently, is the free energy change of the reaction when the products and the reactants are all in their respective standard states. This expression may be substituted by ΔG^0. Hence,

$$\boldsymbol{\Delta G = \Delta G^0 + RT \ln Q_p} \quad \ldots\text{(v)}$$

Where Q_p stands for the reaction quotient of partial pressures of the products and reactants, viz,

$$\frac{(p_L)^l\,(p_M)^m \ldots}{(p_A)^a\,(p_B)^b \ldots}$$

Equation (v) is known as **van't Hoff reaction isotherm**. This gives the free energy change of a reaction at any given temperature, pressure and composition of the reacting system, Q_p is different from K_p. Here the values $p_L, p_M, p_A, p_B \ldots$ etc are not the partial pressures at equilibrium, but for any state. If the partial pressure values correspond to equilibrium state, then Q_p will become equal to K_p. As we have

$$\Delta G° = -RT \ln K_p$$

Substituting for $\Delta G°$ in eq. (v), we have

$$\boldsymbol{\Delta G = -RT \ln K_p + RT \ln Q_p} \quad \ldots\text{(vi)}$$

Equation (v) and equation (vi) are two forms of van't Hoff reaction isotherm.

(ii) Van't Hoff Equation for the Temperature Dependence of Equilibrium Constant (Van't Hoff Reaction Isochore)

The equation for reaction isotherm when the reactants as well as the products are gaseous and are also in their standard states, is represented as

$$\Delta G° = -RT \ln K(p) \quad \ldots\text{(i)}$$

Differentiating with respect to temperature at constant pressure, we have

$$\left\{\frac{\partial\,(\Delta G°)}{\partial T}\right\}_p = -R \ln K_p - RT\,\frac{d\,(\ln K_p)}{dt}$$

Multiplying throughout by T, we get

$$T\left\{\frac{\partial\,(\Delta G°)}{\partial T}\right\} p = -RT \ln K_p - RT^2\,\frac{d\,(\ln K_p)}{dT} \quad \ldots\text{(ii)}$$

Substituting $\Delta G°$ for $-RT \ln K_p$, we have

$$T\left\{\frac{\partial (\Delta G°)}{\partial T}\right\}p = \Delta G° - RT^2 \ln K_p - RT^2 \frac{d (\ln K_p)}{dT} \qquad \text{...(iii)}$$

The well known Gibbs-Helmholtz equation for substances in standard states may be written as

$$\Delta G° = \Delta H° + T\left\{\frac{\partial (\Delta G°)}{\partial T}\right\}p \qquad \text{...(iv)}$$

Comparing equation (iii) and (iv), we get

$$RT^2 \frac{d (\ln K_p)}{dT} = \Delta H°$$

or

$$\frac{d (\ln K_p)}{dT} = \frac{\Delta H°}{RT^2} \qquad \text{...(v)}$$

Equation (v) is known as the van't Hoff's equation. $\Delta H°$ is the enthalpy change for the reaction at constant pressure when the reactants as well as products are in their standard states.

It is well known from experiments that the enthalpy change, ΔH, accompanying a chemical reaction does not vary appreciably with change in partial pressures of the reactants and products. Therefore, we may take $\Delta H°$ as equal to ΔH, where ΔH is the enthalpy change of the reaction whatever may be the partial pressures of the reactants or products. Hence, the van't Hoff equation may be written as

$$\frac{d (\ln K_p)}{dT} = \frac{\Delta H}{RT^2} \qquad \text{...(vi)}$$

Integrating equation (vii) between temperatures T_1 and T_2 at which the equilibrium constants are K'_p and K''_p respectively and assuming that ΔH remains constant over this range of temperature, we get

$$\int_{K'_p}^{K''_p} d (\ln K_p) = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln K''_p - \ln K'_p = \frac{-\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \text{...(vii)}$$

$$\log K''_p - \log K'_p = \log \frac{K''_p}{K'_p} = \frac{\Delta H}{2.303\, R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \text{...(viii)}$$

Knowing the equilibrium constant at a temperature it is possible to calculate the equilibrium constant at another temperature provided the heat of reaction (ΔH) is known.

Alternatively, knowing the equilibrium constants of a reaction at two temperatures, the heat of reaction (ΔH) can be calculated.

Q.6. Describe Clausius clapeyron equation and its application.

Ans.

Clausius-Clapeyron Equation

If the temperature of the liquid is not too near the critical point then we can easily neglect the volume of the liquid (V_L), compared with that of vapour (V_V). In such a case, the equation $\frac{dP}{dT}=\frac{\Delta H_V}{T(V_V-V_L)}$ reduces to equation (1) on replacing P by p. So

$$\frac{dP}{dT}=\frac{\Delta H_V}{TV_V} \quad \text{...(i)}$$

Furthermore, under such conditions the vapour pressure is very small, so it may be assumed that the vapour behave as an ideal gas to which the equation $PV_V=RT$ is applicable.

$$\frac{dP}{dT}=p\cdot\frac{\Delta H_V}{RT^2}$$

or

$$\frac{1}{p}\frac{dP}{dT}=\frac{\Delta H_V}{RT^2}$$

or

$$\frac{d\log p}{dT}=\frac{\Delta H_V}{RT^2} \quad \text{...(ii)}$$

Equation (ii) is sometimes known as **Clausius-Clapeyron** equation and is generally spoken of as first latent heat equation. It was first derived by Clausius (1850) on the thermodynamics basis of Clapeyron equation.

Equation (ii) is valid for evaporation and sublimation processes but not valid for transition between solids or for the melting of solids. Clausius-Clapeyron equation is an approximate equation because the volume of the liquid has been neglected and ideal behavior of the vapour is also taken into account. However equation (ii) has the advantage of greater simplicity because in the calculation of the value dp/dT or dT/dp, it is necessary to know the volumes of the liquid and the vapour.

Integrated form of Clausius-clapeyron equation

Assuming the heat of vaporization to be independent of temperature, if we integrate equation (ii) between the limits T_1 to T_2 (for temperature) and p_1-p_2 (for vapour pressure), we get

$$\int_{p_1}^{p_2} d\log p=\int_{T_1}^{T_2}\frac{\Delta H_V}{RT^2}\,dT$$

or

$$\ln\frac{p_2}{p_1}=\frac{\Delta H_V}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

or

$$2.303\log\frac{p_2}{p_1}=\frac{\Delta H_V}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

or

$$\log\frac{p_2}{p_1}=\frac{\Delta H_V}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \quad \text{...(iii)}$$

If ΔH_V is expressed in cal/mole and $R=1.987$ cal/degree/mole, then equation (iii) becomes

$$\log\frac{p_2}{p_1}=\frac{\Delta H_V}{4.576}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \quad \text{...(iv)}$$

Equation (iv) is the **integrated form of Clausius-Clapeyron equation.** If the integration is carried out indefinitely (without limits) then we can write the vapour pressure equation as (ii) as

$$\log p = -\frac{\Delta H_V}{RT} + C \text{ (contant)} \qquad \text{...(v)}$$

Applications of Clausius-clapeyron equation

1. **Latent heat from vapour pressure data :** Suppose the vapour pressures p_1 and p_2 are determined at two temperature T_1 and T_2 respectively, then it is possible to calculate the molar or specific heat of vaporization. It is also possible to calculate the value of HV graphically. It is clear that if log p is plotted against the reciprocal of the absolute temperature, *i.e.*, $1/T$, then a straight line will be obtained. The slope of this line will be equal to $-\Delta H/R$. So, knowing the value of R, the value of ΔH can thus be easily determined after measuring the slope.

2. Deduction of Trouton's law : Equation (ii) can be written in the form

$$\frac{1}{p}\cdot\frac{pd}{dT} = \frac{\Delta H_V}{RT^2}$$

For liquid vapour equilibrium $\Delta H_V = L_e$, *i.e.*, molar heat evaporation. Hence, the last expression becomes,

$$\frac{1}{p}\cdot\frac{pd}{dT} = \frac{L_e}{RT^2}$$

or

$$\frac{T}{P}\cdot\frac{dP}{dT} = \frac{L_e}{RT} \qquad \text{...(vi)}$$

We know that, $\frac{T}{T_e} = \theta$ and $\frac{P}{P_e} = \pi$

Where P_C and T_C represent the critical pressure and critical temperature, respectively and π, θ are the reduced pressure and reduced temperature, respectively. So equation (vi) becomes

$$\frac{\theta}{\pi}\cdot\frac{d\pi}{d\theta} = \frac{L_e}{RT} \qquad \text{...(vii)}$$

Van der Waals (1888) suggested the empirical relationship,

$$\log\frac{P}{P_e} = k\left[1 - \frac{T_c}{T}\right]$$

Where k is constant which is equal to 3 for many substances. Hence in reduced terms it can be put as,

$$\log\pi = 2.3\,k\left[1 - \frac{1}{\theta}\right] \qquad \text{...(viii)}$$

Differentiating equation (viii) with respect to θ, we get,

$$\frac{d\log\pi}{d\theta} = 2.3\,\frac{k}{\theta^2}$$

or

$$\frac{1}{\pi}\frac{d\pi}{d\theta} = 2.3\,\frac{k}{\theta^2}$$

or
$$\frac{\theta}{\pi}\cdot\frac{d\pi}{d\theta}=2.3\frac{k}{\theta} \qquad \text{...(ix)}$$

From equation (vii) and (ix), we conclude that,

$$\frac{L_e}{RT}=2.3\frac{k}{\theta}$$

or
$$\frac{L_e}{T}=6.9\frac{R}{\theta}$$

If the temperature is taken to be the boiling point T_b, then θ which is T_b/T_c is nearly equal to 0.6 and, therfore,

$$\frac{L_e}{T_b}=23 \qquad \text{...(x)}$$

So, the molar heat of vaporization of a liquid divided by its boiling point on absolute scale, *i.e.*, L_e/T_b is constant and is approximately equal to 23, provided the latent heat is expressed in calories. The fact was first observed by Pictet (1876) and rediscovered by Ramsay (1877) and Trouton (1884) and is commonly known as **Trouton's law**. Some substances which obey Trouton's law are ethyl ether, benzene, propyl acetate, mercury, zinc, potassium chloride etc.

This law is an approximate law. For non-associated substances of molecular weight of about 100, the value $(Le/Tb)=21$, provided the boiling point is not too high. The law breaks down for associated compounds such as water and alcohol and for substances having high boiling points.

At the normal boiling point the vapour of liquid is equal to 1 atm., hence equation (v) becomes

$$\log l=-\frac{\Delta H_V}{4.576\,T_b}+C$$

According to Trounton's law, for many non-associated substances, $\Delta H_v/T_b$ may be taken as equal to 21. Hence,

$$C=\frac{21.0}{4.576}=4.589$$

The expression for the vapour pressure p (in atm) of any substances to which Trouton's law is applicable now becomes,

$$\log p\ (\text{atm})=-\frac{\Delta H_V}{4.576\,T}+4.589$$

UNIT-III

Phase Equilibrium

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. What is phase rule?

Ans. In a heterogeneous system in equilibrium the number of degree of freedom plus the number of phases is equal to the number of components plus 2. This relationship is called phase rule.

Q.2. Write phase rule mathematically.

Ans. $F + P = C + 2$

where, $F \rightarrow$ degree of freedom, $P \rightarrow$ number of phases in the system
$C \rightarrow$ number of components.

Q.3. What do you mean by phases.

Ans. The homogeneous but physically distinct and mechanically separable parts of the heterogeneous system are called phases.

Q.4. How many phases there are in :

$$\mathbf{CaCO_3 \rightleftharpoons CaO + CO_2}$$

Ans. $\underset{\text{solid}}{CaCO_3} \rightleftharpoons \underset{\text{solid}}{CaO} + \underset{\text{gas}}{O_2}$

these are three phases *i.e.*, two solid phases and one of gas.

Q.5. What are components?

Ans. The smallest number of independently variable constituents by means of which the composition of each phase present in the system can be expressed director or in the form of an equation are called components.

Q.6. How many phases are there in water system?

Ans. There are three phases in water system *i.e.*,

$$\underset{\text{(solid)}}{\text{Ice}} \rightleftharpoons \underset{\text{(liquid)}}{\text{Water}} \rightleftharpoons \underset{\text{(gas)}}{\text{Vapour}}$$

Q.7. How many phases the sulphur system contains.

Ans. The sulphur system consists four phases *i.e.*, rhombic, monoclinic, liquid and vapour.

Q.8. What is degree of freedom?

Ans. The minimum number of independently variable factors *i.e.*, temperature, pressure and composition of phases must be arbitrary fixed in order that the conditions of the system may be completely defined are known as degrees of freedom.

Q.9. How many phases are there in following :

$$NH_{Cl} \rightleftharpoons NH_4Cl \rightleftharpoons NH_3 + HCl$$

Ans. There are four phases :

$$\underset{\text{solid}}{NH_4Cl} \rightleftharpoons \underset{\text{liquid}}{NH_4Cl} \rightleftharpoons \underset{\text{gas}}{NH_3} + \underset{\text{gas}}{HCl}$$

Q.10. How many components are in Zn.Mg system.

Ans. 2.

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What do you mean by phase and degree of freedom?

Ans.

Phases

It is defined as homogeneous part of a system which is physically and chemically different from other part also it is mechanically separable from other part of the system. Completely miscible gas and liquids form a singles phase while immiscible system give different phases *i.e.*, solid + liquid, solid + gas, have two component. Phases are denoted by P.

Degree of Freedom

It is defined as the no. of independent variables such as temperature, pressure and concentration which must be sepecified in order to define the system completely. It is denoted by F greater the no. of component C, greater the degree of freedom F.

Greater the no. of phase P, smaller the number of degree of freedom F. Degree of freedom as also known as variance.

Q.2. Write a short note on components.

Ans.

Components

The number of components of a system at equilibrium, the minimum number of independent variable constitutions (chemical species) which are required to express quantitavely the composition of each and every phase either directly or in terms of chemical equation is called components or denoted by C. In the chemical equation negative and zero signs being permitted.

Example : (i) Water system consist of the equilibrium.

$$\underset{\text{(Solid)}}{\text{Ice}} = \underset{\text{(Liquid)}}{\text{Water}} = \underset{\text{(Gasecus)}}{\text{Vapour}}$$

This system consists of one component only, *.e.*, it is a one component system because the composition of each of the three phases present can be directly expressed as H_2O.

(ii) Sulphur system consisting of four phases : Monoclinic (s), Rhombic (s), Liquid (L) and vapors (g) is also one component system because the composition of each phase can be expressed in term of one constituent sulphur.

The no. of component is calculate by :

$$C = S - E - R$$

Where, S = Total no. of constituents or species.

E = No. of equation representing equilibrium between the constituents.

R = No. of restrictions for electrical neutrality.

Example : Na_2So_4 -H_2O

(a) Assuming no dissociation

$S = 2$

$E = 0$ (No chemical reaction/equilibrium)

$R = 0$ (No. restriction of electrical neutrality or material balance

$C = S - E - R = 2 - 0 - 0 = 2$. Thus no. of components $= 2$.

(b) Assuming complete dissociation of the salt.

$S = 3\ (Na^+, SO_4^{2-}$ and $H_2O)$

$E = 0$

$R = 1$ (For electrical neutrality, $2Na^+ = SO_4^{2-}$)

$C = S - E - R = 3 - 0 - 1 = 2$. Thus, no. of components $= 2$.

(c) Assuming dissociation of H_2O also.

$S = 6\ (Na_2SO_4, Na^+, SO_4^{--}, H_2O, H^+, OH^-)$

$E = 2\ (Na_2SO_4 \Rightarrow 2Na^+ + SO_4^{--}$ and $H_2O \Rightarrow H^+ + OH^-)$

$R = 2\ (2Na^+ = SO_4^{2-}$ *i.e.*, number of moles of Na^+ 2X No. of moles of SO_4^{2-} and $H^+ = OH^-)$

$C = S - E - R = 6 - 2 - 2 = 2$.

Thus, no. of components $= 2$.

Q.3. Derive the Gibbs phase rule.

Ans.

Derivation of Gibbs Phase Rule

Consider a heterogeneous system in equilibrium consisting of C, components distributed in P phase. The Degree of freedom of the system are equal to the number of independent variable which must be fixed arbitrarily to define the system completely. The number of such variable is equal to the total number of variable minus the number of variable which are defined automatically by virtue of the system being in equilibrium.

At equilibrium, each phase has the same temperature and pressure, so Ibere is one temperature variable and one pressure variable for the whole system. So, these variables total two only. The number of composition (or concentration) variables, however, is much more. In order to define the composition of each phase, it is necessary to mention(C-I) composition variables, because the composition of the remaining component may be obtained by difference. For P phases, thus, the total number of concentration or composition variables will be P(C-1).

Total number of variables = P(C-1) for composition + 1 for temperature + 1 for pressure

According to thermodynamics when a heterogeneous system is in equilibrium, at constant pressure and temperature, the chemical potential (μ) of any given component must be the same in every phase. Therefore, if there is one component in three phases *x*, *y* and *z* and one of these phases, say x is referred to as standard phase, then this fact may be represented in the form of two equations :

So, for each component in equilibrium in three phases, two equations are known. In general, therefore, for each component in P phases, (P-1) equations are known, For C components, thus the number of equations or variables that are known from the conditions of equilibrium are C (P −1).

Since chemical potential is a function of pressure, temperature and concentration, it means that each equation represents one variable.

Therefore, the number of unknown variables (which should be fixed) or degree of freedom

$$F = \text{number of variable- number of equations}$$

$$F = [P(C-1)+2]-[C(P-1)] \text{ or } F = C-P+2, \ldots$$

This equation is the phase rule of Gibbs.

Q.4. What is phase equilibrium?

Ans.

Phase Equilibrium

A System is in equilibrium is the properties like temperature, composition etc. of the various phases do not undergo any change with time.

It is of two types :

(i) True equilibrium

(ii) Metastable equilibrium

(i) **True Equilibrium :** It defined as : If the same state can be achieved by approach from either direction. For example, the equilibrium between ice and water at I atm. Pressure and 0°C is a true equilibrium, because it can attained by melting of ice or by freezing of water.

(ii) **Metastable equilibrium :** If the state of a system can be attained only from one direction and that too by very careful change of conditions, it is called a state of metastable equilibrium. For example, water at 2°C can be obtained only by very careful cooling of liquid water but not by melting of ice. Hence water at −2°C is said to be in a state of metastable equilibrium.

Q.5. Write the criteria of phase equilibrium.

Ans.

Criteria of Phase Equilibrium

There are three equlibria that exist in phase equilibria is a multi component system.

(i) **Thermal Equilibria :** The temperature is every part of the system must be same as otherwise heat may flow from one part of the system to another. Suppose a system consist of two phase A and B with temperature T_A and T_B respectively.

At equilibrium, let a small amount of heat dq. flows from phase A to phase B.

Then, Entropy change of phase A $(dS_A) = -\dfrac{dq}{T_A}$

Entropy change of Phase B $(dS_B) = -\dfrac{dq}{T_B}$

So, Total entropy change of system $dS = \dfrac{dq}{T_A} + \dfrac{dq}{T_B}$

The condition for equilibrium is terms of entropy change is $(dS)\,E.V. = 0$.

i.e.,
$$-\frac{dq}{T_A} + \frac{dq}{T_B} = 0 \text{ or } \frac{dq}{T_A} + \frac{dq}{T_B} \text{ or } T_A = T_B$$

(ii) **Mechanic Equilibrium :** The equilibrium where the pressure in every part of the system must be same as otherwise matter may flow form one part of the system to another. In an as isolated system containing two phase in equilibrium at constant volume and temperature.

A small amount of matter flow from phase A to B so, that volume phase A decrease by small volume dV and volume of phase B increase by small volume d_V.

The pressures of two phases are P_A and P_B respectively. So, change in Helmoltz free energy of phase $A\ (dA_A) = P_A dv$.

Change in Helmoltz free energy of phase $B\ (dA_B) = P_B dV$

But at equilibrium $(dA)\ V = 0$.

$$dA = dA_A + dA_B = -P_A dV + P_B dV = 0 \text{ or } P_A = P_B$$

(iii) **Chemical Equilibrium :** At equilibrium, the chemical potential of any component in all the phases must be same. This is called **Thermodynamic criteria for phase equilibrium.** For a solution(or a phases containing a number of constituents, the chemical potential of any component is the increase of decrease of free energy that takes place, at constant temperature and pressure, for the addition or removal of one mole of that component, keeping the amount of all other components constant it is usually represented by 'μ').

Q.6. Write the types of two component systems.

Ans.

Types of two Component Systems

Broadly, there are three types of two-component system involving solid-liquid equilibria.

Type I : Those in which the two components do not react with each other but simply mix into each other in the molten slate or in the solution. Examples of such system are lead-silver system and KI-H_2O system.

Type II : Those in which the components react to form a compound with congruent melting point. These are those system in which the two pure components react to form a compound which is stable up to its melting point At the melting point, it melts to give a liquid of the same composition as that of the solid compound. The compound formed is then said to have a congruent melting point.

For example in $FeCl_3$-H_2O system, each hydrate formed is stable up to the melting point and possesses a congruent melting point.

Type III : Those in which the components react to form a compound with incongruent melting point. These are those two-compound formed does not remain stable up to the melting point. On heating, it starts decomposing before the melting point to give a new solid phase and a solution with composition different from that of the solid phase. When this happens, the compound is said to undergo a transition or peritectic (reaction and is said to have incongruent melting point. In general, a peritectic reaction may be represented by the equation $C_2 = C_1 +$ (solution, molten).

C_2 represents is the compound formed as a result of reaction between the two pure components and C_1 is the new compound (or a pure consitituent) formed as a result of decomposition of compound C_2 below its melting point. An example of this type of system is Na_2SO_4-H_2O system in which the hydrates formed undergo peritectic reaction.

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. Discuss the phase diagram of water system.

Ans.

Phase Diagram of Water System

The system consists of three phases.

$$\underset{(s)}{\text{Ice (solid)}} \rightleftharpoons \underset{(i)}{\text{Water (liquid)}} + \underset{(g)}{\text{Vapour (gas)}}$$

These three single phases may occur in four possible combinations in equilibrium as :

(i) Liquid $\rightleftharpoons$ Vapour

(ii) Solid $\rightleftharpoons$ Vapour

(iii) Solid $\rightleftharpoons$ Liquid

(iv) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

The number of phases that can exist in equilibrium at any point depends upon the conditions of temperature and pressure. These conditions have been determined experimentally and a phase diagram is constructed by plotting pressure against temperature (Fig. 1). The phase diagram consists of :

(i) Three stable curves OA, OB, OC and one metastable curve OA.

(ii) Three areas and

(iii) Definite point, O.

These are separately discussed as under :

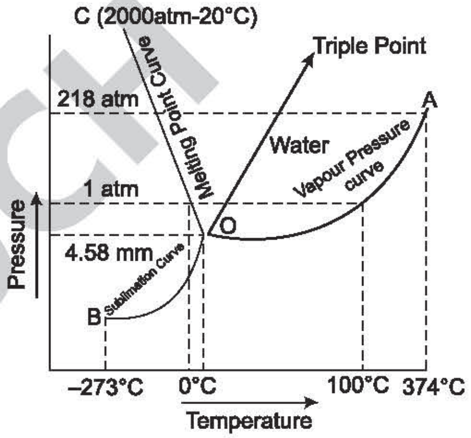


Fig. 1 : Water System

1. **Curves (i) OA :** This is vapour pressure curve of water. It represents the equilibrium between liquid water and vapour at different temperature. At any point on the curve, the two phases are present. The curve starts from the point *O*, the freezing point of water and ends at *A*, the critical temperature (374°C) beyond which the two phases merge into each other. Consider any point on the curve. For a fixed value of pressure, temperature has also a fixed value. If by keeping the pressure constant, an attempt is made to raise the temperature then the liquid phase will disappear and if temperature is lowered then the vapour phase will disappear. Thus, to define the system completely at any time, it is necessary to mention either temperature or pressure. In other words,

pressure being fixed. Therefore, water-vapour system is univariant, or it has one degree of freedom. It also follows from the phase rule equation.

$$F = C - P + 2$$
$$F = 1 - 2 + 2 = 1$$

(ii) **OA :** The dotted curve OA : a continuation of curve OA represents the vapour pressure curve of super-cooled water. It is metastable curve. On being disturbed, the super cooled phase at once changes to solid ice and curve merges into OB.

(iii) **OB :** It is the sublimation curve or the vapour pressure curve of ice. It gives values of temperature and pressure at which ice and vapours can exist together. It is obtained by studying the effect of pressure on the freezing point of water. The curve starts from the point O, the freezing point of water and ends at B (– 273°C). As temperature decreases, the vapour pressure of ice tends to become negligible. We find that for a particular temperature, there can be one and only one pressure value and vice versa. In other words, ice-vapour system is univariant, or has one degree of freedom.

(iv) **OC :** It is melting point curve and represents the equilibrium between ice and liquid water at various pressures. In other words, it shows the effect of pressure on the melting point of ice. It should be noted that the line OC is inclined towards the pressure axis. The slope of the curve OC clearly indicates that melting point of ice is lowered by increase of pressure. There is, however, no limit for the curve OC. It goes up to a point corresponding to 2000 atmospshere and – 20°C. At this point, one type of ice changes into another solid modification but the solid-liquid equilibrium still remains.

At any point on the curve OC, two phases (ice and liquid water) are present in equilibrium. Hence the system is univariant, or degree of freedom is one.

2. **Areas :** The areas, *i.e.*, the regions bounded by two lines give the conditions of temperature and pressure under which the single phase *i.e.*, ice or liquid water or vapour is capable of stable existence. Area below AOB has water vapour, are BOC has ice and area COA has liquid water. These areas are bivariant because to locate any point in the area, temperature as well as pressure must be fixed, thus indicating two degrees of freedom. This also follows from phase rule equation.

$$\mathrm{F} = C - P + 2$$
$$\mathrm{F} = 1 - 1 + 2 = 2$$

3. **Triple point :** It is a point where the three curves OA, OB, OC meet. At this point the three phases-**ices, water and vapour** are in equilibrium. It should be noted that it is only a point indicating that there is only one set of conditions under which it is possible for the three phases to exist together. The point O is a self-defined point corresponding to definite temperature of 0.0098°C and a definite pressure of 4.58 mm. If either pressure or temperature is changed, then one of the three phases will disappear. Since on changing either pressure or temperature one of the phases disappear, therefore, the system at the point O has no degree of freedom, that is, it is invariant or nonvariant. The same result follows from phase rule equation.

$$\mathrm{F} = C - P + 2$$
$$\mathrm{F} = 1 - 3 + 2 + 0.$$

Q.2. Discuss the phase diagram of CO_2 system.

Ans. Phase Diagram of Carbon Dioxide System

Phase diagram of carbon dioxide system resembles that of water system with some differences.

The phase diagram for carbon dioxide system is shown in Fig. 2. It has three distinct areas in which carbon dioxide can exist either as solid, liquid or gas.

Areas : Area on the R.H.S. of the curve ABD consists of vapour phase. Area of the curve CBD consists of the liquid phase, while the area on the L.H.S. of the curve ABC consists of solid phase.

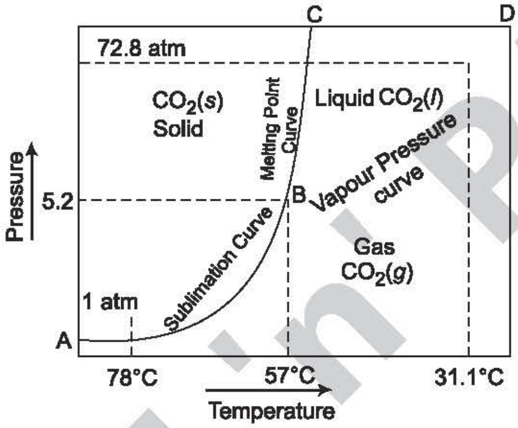


Fig. 2 : The phase diagram for the carbon dioxide system

Curves : AB is the sublimation curve along which solid carbon dioxide is in equilibrium with the gas. BD is the vaporization curve along which liquid carbon dioxide is in equlibrium with the gas. This curves ends at 31.1°C, the critical temperature of CO_2 and corresponding to pressure of 72.8 atmospheres. The curve BC is the fusion curve along which solid and liquid carbon dioxide are in equilibrium with each other.

Point : B is the triple point at which all the three phases of carbon dioxide co-exist in equilibrium with one another. The temperature of the system at this point is – 57°C while the pressure is 5.2 atm. A slight variation in temperature or pressure at this point may result in the disappearance of one of the two phase. For example, a slight increase in temperature will result in the disappearance of the solid phase and the equilibrium will shift along the curve BD while a slight decrease in temperature will result in the disappearance of the liquid phase and the equilibrium will shift along the curve BA. Keeping the temperature constant, if the pressure is increased, the gaseous phase will disappear and the equilibrium will shift along the curve BC.

The phase diagram of carbon dioxide resembles that of water in showing three distinct areas for solid, liquid and gaseous phases. But it differs from the latter in several respects. In the first place, the melting point slopes away from the pressure axis. This indicates that increase of pressure raises the melting point of solid carbon dioxide.

The second difference is that solid carbon dioxide can exist in equilibrium with its liquid only at a very high pressure equal to 5.2 atm. This is unlike the water system in which ice and water can exist in equiliibrium even at a very low pressure equal to 4.58 mm of Hg (Refer to phase diagram of water).

The third difference is that the vapour pressure of solid carbon dioxide even at extremely low temperature is very high and many times higher than that of ice.

Q.3. Discuss the phase diagram of Bi-Cd system.

Ans. Phase Diagram of Bismuth-Cadmium (Bi-Cd) System

This is an example of a two component system which forms a simple eutectic. The various phases that may be present are (I) solid bismuth (ii) solid cadmium (iii) solution of bismuth in cadmium or vice versa in themolten stale (iv) vapour.

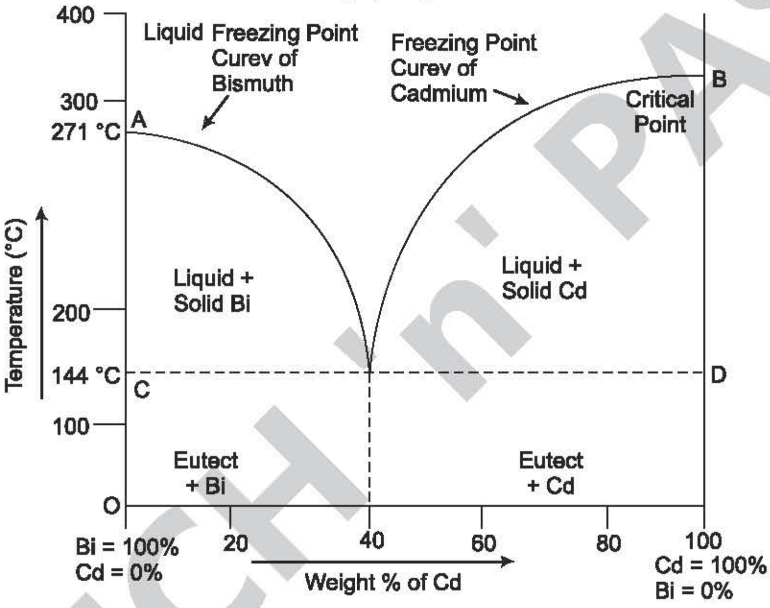


Fig. 3 : Phase diagram Bi-Cd system curves

Curve AO : It represents the freezing point curve of bismuth to which different amounts of cadmium are added. The point *A* represents the melting point, or freezing point of pure bismuth (271°C). We find that the melting point (or) free/mi point of bismuth is lowered gradually buy addition of cadium into it. The added cadmium goes into the solution and the separation of bismuth occurs till the point) is reach. At this point, no more cadmium goes into the solution as the solution becomes saturated with cadmium and hence the melting point of bismuth does not fall further. Thus the point *O* represents the composition with lowest melting (point144°C). Point *O* represents the eutectic point. Along the curve *AO*, two phases in equilibrium are solid bismuth and liquid melt (neglecting the vapour phase). Therefore the system is univariant as shown below.

Curve BO : This is the freezing point curve of cadmium to which different amounts of bismuth are added. The point B represent the melting point or freezing point of pure cadmium (321 V). We find that melting point of cadmium decreases as more and more of bismuth is added into it the added bismuth goes into the solution and separation of solid cadmium takes place. This continues till the point *O* is reached. At this point no more bismuth goes into the solution and the solution is said to have become saturated with bismuth.

Hence, the melting point does not fall any longer.

Along the curve two Phases solid cadmium and liquid melt are in equilibrium.

Therefore,

$$F = C - P + 1 = 2 + 1 = 1 \; i.e., \text{ the system is univariant.}$$

It may be noted that the point –, on me curves AO and BO represent the initial freezing points while the points on the line CD represent the final freezing points. It may also be noted that the curve AO is not only freezing point curve of bismuth but may also be considered as solubility curve of bismuth because the points on this curve represent the solubilities of bismuth in the molten cadmium at various temperatures. Similarly, the curve BO may also be considered as the solubility curve of cadmium.

Eutectic Point O : This is the point where the two curves AO and BO meet. At this point solid bismuth and solid cadmium are in equilibrium with the melt, *i.e.*, three phases are present degree of freedom at the point O is zero.

$$F = C - P + 1 = 2 - 3 + 1 = 0$$

The point O represents the lowest possible temperature (144°C) below a liquid phase cannot exist and above which the liquid phase cannot be enriched in either component by freezing out the other component. Such a liquid mixture of two components which has the lowest freezing point compared to all other liquid mixtures is called emetic mixture. This mixture freezes out completely at constant as solid phases in the same proportion in which they were present in the liquid phase. The temperature corresponding point O is called I he eutectic temperature. This is always lower than the melting points of the either component. In this system, eutectic mixture (containing about 40% Cd and 60% Bi by mass) melts at 144°C, which is lower than the melting point of bismuth 271°C of cadmium 321°C.

Q.4. Discuss the phase diagram of Pb-As system.

Ans.

Phase Diagram of Pb-Ag System

Pb-Ag system is four phase and two component systems for which a complete phase diagram can be represented as :

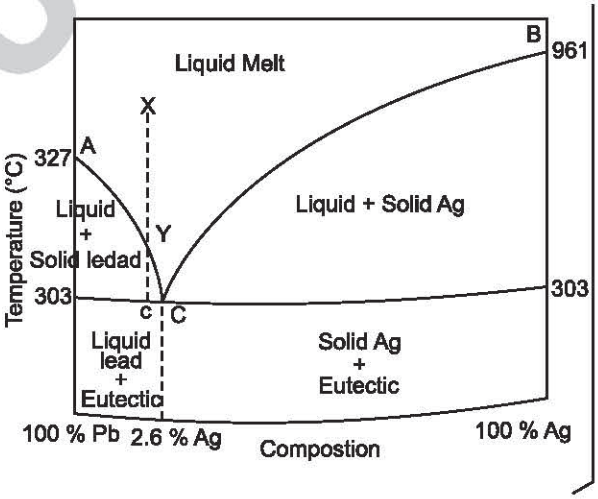


Fig. 4 : Phase diagram of Pb-Ag system

According to the above phase diagram the various regions, curves, eutectic point, eutectic T and eutectic composition in the phase diagrams of Pb-Ag system can be defined as :

Various regions : Different types of the regions present in the two component Pb-Ag system are given as :

(a) Region above the ACB : Liquid solution of Pb and Ag.

(b) Region within the ACD : Solid Pb and Solution of Ag in Pb.

(c) Region within the BCD : Solid Ag and the solution of Pb in Ag.

Various curves :

1. Curve Ac indicates the freezing curve of Pb with the addition of Ag in which point A indicates the freezing point of pure Pb.

   In the curve Ac, $C = 2$, $P = 2$.

   So, according to reduced phase rule;

   $$F = C - P + 1$$
   $$F = 2 - 2 + 1 \Rightarrow F = 1$$

   i.e., System in the curve AC will be univarient.

2. Curve *BC* indicates the freezing curve of Ag with the addition of Pb, in which point B indicates the freezing point of pure Ag.

Eutactic point, Eutactic temperature and Eutactic composition : In the phase diagram of Pb-Ag system the melting point of *AC* and *BC* curves is known as eutectic point. Temperature and composition corresponding to this eutectic point are known as eutectic temperature (303°C) and eutectic composition (97.4% Pb + 2.6% Ag) for Pb-Ag system.

●

UNIT-IV

Kinetic Theory of Gases

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Name the three physical states of matter.

Ans. Solid, liquid and gas.

Q.2. Can a substance exist in all the three states of matter? Give an example.

Ans. Yes, water.

Q.3. What is the relation between mass and number of moles of a gas?

Ans. $n = \frac{m}{M}$

Q.4. Express one atm pressure in terms of the height of mercury column.

Ans. 76 cm and 760 mm Hg.

Q.5. What is the SI unit of pressure?

Ans. Pa or Nm^{-2}

Q.6. Name the apparatus used for the measurement of the pressure of a gas.

Ans. Manometer

Q.7. What is the shape of the curve obtained on plotting P against PV at constant temperature for an ideal gas?

Ans. Straight line parallel to pressure axis

Q.8. Which law is signified by the relation $\frac{V_1}{T_1} = \frac{V_2}{T_2}$?

Ans. Charles' law

Q.9. Name the scientist who introduced absolute scale of temperature.

Ans. Lord Kelvin

Q.10. What is the general unit of gas constant R?

Ans. Energy $\text{deg}^{-1}\text{mol}^{-1}$

Q.11. What happens when a jar full of H_2 gas is placed inverted over a jar containing Cl_2 gas?

Ans. The two gases diffuse into each other and the mixture of gases in the two jars acquire the colour of chlorine.

Q.12. What is the measure of average kinetic energy of a gas?

Ans. Absolute temperature.

Q.13. Is the excluded volume of a real gas equal to the actual volume of the molecules of a gas?

Ans. No, the excluded volume of a real gas is four times the actual volume of the molecules.

Q.14. Under what conditions of temperature and pressure does a real gas behave almost similarly to an ideal gas?

Ans. At low pressures and high temperatures.

Q.15. Write the formula of average velocity.

Ans. $x = \sqrt{\frac{QRT}{\pi M}}$

Q.16. Write the formula of root mean square velocity.

Ans. $v = \sqrt{\frac{3RT}{M}}$

Q.17. Write the formula of most probable velocity.

Ans. $\alpha = \sqrt{\frac{2RT}{M}}$

Q.18. Write the relationship in three types of velocities.

Ans. Average velocity = 0.9213 × RMS velocity

Most probable velocity $= \sqrt{\frac{2}{3}} \times$ RMS velocity

i.e., $\alpha : x : v = 1 : 1.2Q : 1.224$

Q.19. What is collision frequency?

Ans. Number of collisions experienced by molecules per C.C. per sec. is called collision frequency.

Q.20. Write the formulae of collision frequency.

Ans. $c = \frac{n}{2}\sqrt{\frac{\pi x \sigma^2 N^2}{22}}$

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. Write the fundamental postulates of kinetic theory of gas.

Ans.

Kinetic theory of gases

The kinetic theory of gases is the study that relates the microscopic properties of gas molecules (like speed, momentum, kinetic energies etc.)with the macroscopic properties of gas molecules (like pressure, temperature and volume).

Fundamental postulates of kinetic theory

1. The molecules of a gas are considered to be rigid, perfectly elastic, identical in all respects. They are solid spheres. Their size is negligible compared to intermolecular distances.
2. The molecules are in random motion in all directions with all possible velocities.

3. The molecules collide with each other and with the walls of the container. At each collision, velocity changes but the molecular density is constant in steady state.
4. As the collisions are perfectly elastic, there is no force of attraction or repulsion between the molecules. Thus the energy is only kinetic.
5. Between any two successive collisions, molecules travel with uniform velocity along a straight line.

Q.2. Write short notes on :

(i) Root mean square velocity.

(ii) Average velocity.

(iii) Most proabable velocity.

Ans.

(i) Root Mean Square Velocity

Velocity *v* which if possessed by each of the *n* molecules of the gas leads to correct calculation of total kinetic energy of the gas is known as root mean square velocity.

$$\text{Total kinetic energy} = n\frac{1}{2}mv^2 \qquad \text{...(1)}$$

We will proceed to test the validity of the above equation (2) mathematically.

Out of the total number of molecules n contained in the given sample of gas, let n_1, molecules have velocity v_1, n_2 molecules have velocity v_2 and so on then,

$$n = n_1 + n_2 + n_3 \qquad \text{...(2)}$$

the total kinetic energy KE of the n molecules is the sum of the kinetic energies of the individual molecules.

Thus
$$KE = n_1 \times \frac{1}{2}m_1v_1^2 + n_2\frac{1}{2}m_2v_2^2 + \ldots \qquad \text{...(3)}$$

$$\frac{1}{2}nv^2 = n_1 \times \frac{1}{2}m_1v_1^2 + n_2\frac{1}{2}m_2v_2^2 + \ldots \qquad \text{...(4)}$$

$$v^2 = \frac{n_1v_1^2 + n_2v_2 sup2 + \ldots}{n} \qquad \text{...(5)}$$

thus v^2 is the mean of squares of the velocities of all the n molecules in the gas and is termed as mean square velocity.

So,
$$v = \sqrt{\frac{n_1v_1^2 + n_2v_2^2 + \ldots}{n}} \qquad \text{...(6)}$$

Here *v* is root of the mean of squares of velocities and is called root mean square velocity and is often written simply as rms velocity. Its value can be calculated as

$$v_{\text{rms}} = \sqrt{3RT / M} \qquad \text{...(7)}$$

(ii) Average Velocity

The average velocity is given by the arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature.

Suppose one molecule is moving with velocity v_1, one molecule with velocity v_2, third molecule with velocity v_3 and so on. Then total velocity will be

$$v_1 + v_2 + v_3 \ldots.$$

There are total of n molecules

The $$v_a = \frac{v_1 + v_2 + v_3 \dots}{n}$$

its value can be calculated as $$v_a = \left(\frac{2RT}{M}\right)^{1/2} \qquad \dots(8)$$

This is **average velocity** represented by v_a.

(iii) Most Probable Velocity

Velocity possessed by most number of molecules is known as most probable velocity.

Most probable velocity $$v_{mp} = (8RT/\pi M)^{1/2} \qquad \dots(9)$$

It is found that

$$v_{rms} > v_a > v_{mp}$$

$$v_{rms} : v_a : v_{mp} = 1.0 : 0.92 : 0.82$$

Q.3. Write short note on liquification of gases.

Ans.

Liquification of Gases

A gas may be liquefied by cooling it below its critical temperature followed by application of suitable pressure on it. The cooling of a gas is usually carried out by making use of the following two principles.

1. **Joule-Thomson effect :** When a highly compressed gas, at a temperature below its inversion temperature, is passed through a throttle (a porous plug or jet) from a region of high pressure to a region of low pressure under adiabatic conditions, it suffers a fall in temperature. This phenomenon is called Joule-Thomson effect and is widely used for the liquefaction of gases.
2. **Adiabatic expansion involving mechanical work :** When a gas is subjected to adiabatic expansion involving mechanical work, it loses some of its kinetic energy and records a fall in temperature.

There are several methods used for the liquefaction of gases. Among these, the two important ones used for the liquefaction of air have been described below.

1. **Linde's method :** This method makes use of Joule-Thomson effect and is used for the liquefaction of air. The apparatus used in this method is shown in Fig. 1. Pure and dry air is introduced into a compressor where it is compressed to about 200 atmosphere. It is then passed through a pipe cooled by a refrigerating liquid such as liquid ammonia which removes the heat of compression. The compressed air is then passed through a spiral pipe having a jet at its end and fitted in an insulated chamber. As the compressed air passes through the jet, it suffers Joule-Thomson expansion resulting in a considerable decrease in its temperature. The expanded air moves up the chamber and cools the fresh air coming through the spiral tube. It is then collected through a pipe and again sent to the compressor. The process is repeated over and over again when the air gets sufficiently cooled and gets liquefied.

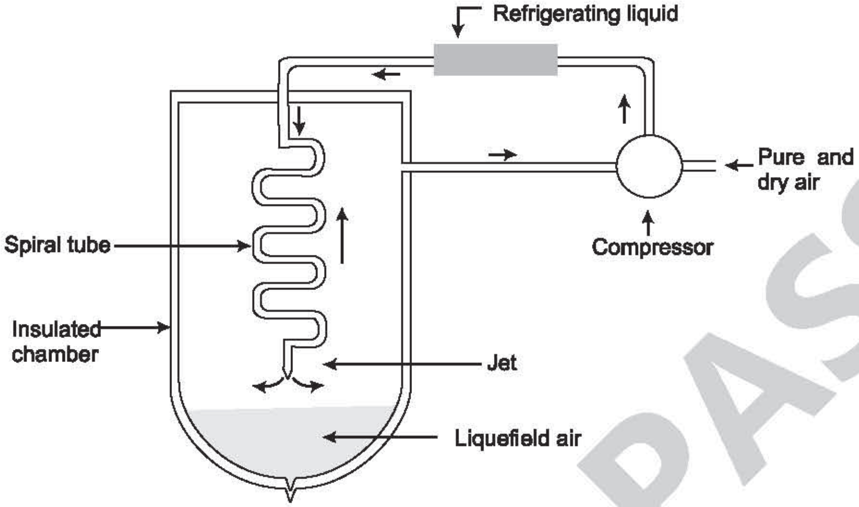


Fig. 1 : Linde's method for liquefaction of air

2. **Claude's method :** This method makes use of both Joule-Thomson effect and adiabatic expansion of the gas involving mechanical work and is more efficient as compared to Claude's method.

The apparatus used in this method is shown in Fig. 2. Pure and dry air is admitted into the compressor where it is compressed to about 200 atmosphere. It is then cooled by a refrigerating liquid to remove the heat of compression. The compressed gas is taken to an insulated chamber through a tube. Here, it is bifurcated into two parts. One part is passed through a spiral tube having a jet at the end, where it suffers Joule-Thomson expansion and records a fall in temperature. The other part is taken to the cylinder of an engine, where it does mechanical work by pushing back the piston and gets cooled. It then enters the insulated chamber and mixes with the air coming out of the jet. It then cools the pipe carrying the incoming air. The cooled air is collected and taken to the compressor again. The entire process is repeated over and over again when the air gets sufficiently cooled and gets liquefied.

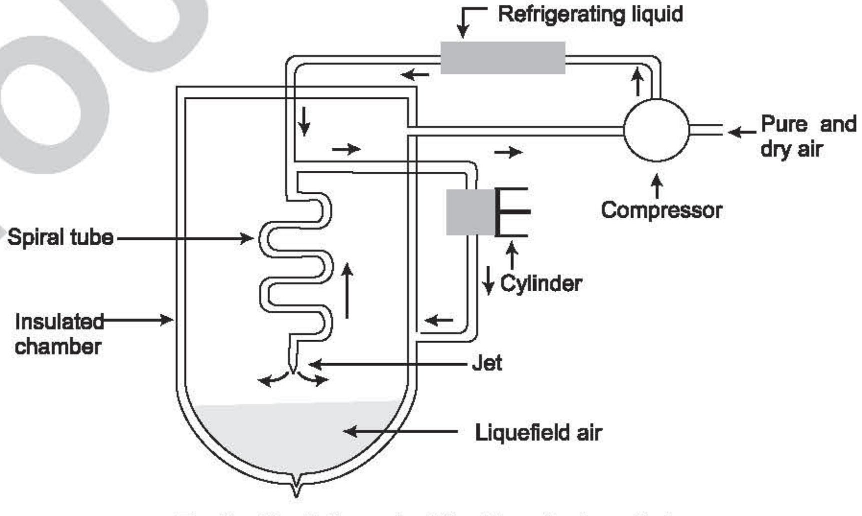


Fig. 2 : Claude's method for liquefaction of air.

Q.4. What do you mean by collision number.

Ans.

Collision Number

The kinetic theory of gases treats molecule as point masses. When two such molecules approach each other, a point is reached at which they cannot come closer beyond a certain distance.

The closest distance between the centres of the two molecules taking part in collision is called the collision diameter. It is denoted by σ.

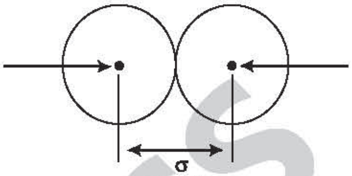


Fig. 3

Whenever the distance between the centres of two molecules is σ, a collision occurs. The collision diameter can be determined from viscosity measurements. The collision diameter of hydrogen is 2.74 Å and that of oxygen is 3.61 Å.

Q.5. Calculate the root mean square velocity, average velocity and the most probable velocity for oxygen molecules at 0°C.

Ans. Root mean square velocity is expressed as

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 273}{32 \times 10^{-3}}}$$

$$= 4.613 \times 10^{2} \text{ m/s}$$

The average velocity is given by

$$v_a = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 273}{3.143 \times 32 \times 10^{-3}}}$$

$$= 4.249 \times 10^{2} \text{ m/s}$$

The most probable velocity is given by

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 273}{32 \times 10^{-3}}}$$

$$= 3.766 \times 10^{2} \text{ m/s.}$$

Q.6. Calculate the total kinetic energy of 55 g of CO_2 / gas at 27°C.

Ans. Kinetic energy per mole of a gas $= \frac{3}{2} RT$

$$\bar{E}_k = \frac{3}{2} \times 8.314 \times 300$$

$$= 3741.3 \text{ J mol}^{-1}$$

Number of moles in 55 of $CO_2 = \frac{55}{44} = \frac{5}{4}$ moles

Thus, Total K.E. of $CO_2 = 3741.3 = \frac{5}{4}$

$$= 4676.63 \text{ J}$$

Q.7. One mode of CO_2 was found to occupy a volume of 1.32 litres at 48°C. Calculate pressure from (i) the ideal gas equation, and (ii) the van der Waal's equation ($a = 3.59$ atm lit^2 mol^{-2}, $b = 4.27 \times 10^{-2}$ lit mol^{-2} and $R = 0.082$ lit atm deg^{-1}mol^{-1}).

Ans. (i) For 1 mole of an ideal gas

$$PV = RT \quad \therefore P = \frac{RT}{V}$$

or
$$P = \frac{0.082 \text{ lit atm} \times 321}{1.32}$$

$$= 19.9 \text{ atm.}$$

(ii) According to van der Waal's equation for 1 mole of the gas,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

or
$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$= \frac{0.082 \times 321}{1.32 - 0.0427} - \frac{3.59}{(1.32)^2}$$

$$= 18.5 \text{ atm}$$

Q.8. The critical temperature and critical density of CO_2 are 304 K and 0.45 g/cc. Calculate, van der Waal's constants '*a*' and '*b*'.

Ans. Critical Volume,
$$V_c = \frac{M}{d_c} = \frac{44 \text{ g mol}^{-1}}{0.45 \text{ g cm}^3}$$

$$= 97.8 \text{ cm}^3 \text{ mol}^{-1} = 9.78 \times 10^{-2} \text{ lit mol}^{-1}$$

$$b = \frac{V_c}{3} = \frac{9.78 \times 10^{-2}}{3} \text{ lit mol}^{-1} = 3.26 \times 10^{-2} \text{ lit mol}^{-1}$$

Further,
$$a = \frac{27bRT_c}{8}$$

$$= \frac{27 \times 3.26 \times 10^{-2} \times 0.082 \times 304}{8}$$

$$= 2.74 \text{ lit}^2 \text{ atms mol}^{-2}$$

Q.9. Find the root mean square velocity and average velocity of oxygen molecules at N.T.P. The density of oxygen is 1.429 g per lit. at N.T.P.

Ans. Root mean square velocity may be given by

$$v = \sqrt{\frac{3P}{d}}$$

$$P = 1 \text{ atm} = 0.76 \times 13.6 \times 10^3 \times 9.81 \text{ Nm}^{-2}$$

$$d = 1.429\ \text{g/lit.} = \frac{1.429}{1000}\ \text{g/cc}$$

$$= \frac{1.429}{1000 \times 1000}\ \text{kg}/10^{-6}\ \text{m}^3$$

$$= 1.429\ \text{kg/m}^3$$

$$\therefore \qquad v = \sqrt{\frac{3 \times 0.76 \times 13.6 \times 10^3 \times 9.81}{1.429}}$$

$$= 461.2\ \text{m/s}$$

Now, average velocity is given by

$$v_a = 0.92 \times v$$

$$= 0.92 \times 61.2$$

$$= 424.56\ \text{m/s}$$

Q.10. The density of carbon monoxide at 0°C and 1 atm pressure is 1.2504 kg m^{-3}. Calculate (a) the root mean square speed (b) the average speed, and (c) the most probable speed.

Ans. We know,

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

$$= \sqrt{\frac{3\,(1.013 \times 10^5\ \text{kg m}^{-1}\text{s}^{-2})}{1.2504\ \text{kg m}^{-3}}}$$

$$= 493\ \text{ms}^{-1}$$

$$v_a = 0.92 \times v = 0.92 \times 493$$

$$= 453.6\ \text{ms}^{-1}$$

$$v_{mp} = 0.82 \times v = 0.82 \times 493$$

$$= 404.3\ \text{ms}^{-1}$$

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. Discuss the causes of deviation from ideal gas behaviour. How they are accounted for in van der Walls equation.

Or **Write a note on :**

(i) Deviation from ideal gas behaviour.

(ii) van der Walls equation of state.

Ans.

Deviation from Ideal Behaviour

An ideal gas is one which obeys the gas laws for the equation $PV = RT$ at all pressures and temperatures. However no gas is ideal. They approach perfection as the temperature gets farther from their boiling points. Thus the gases H_2, N_2 and CO_2 which fail to obey the ideal-gas equation are termed as non ideal or real gases.

The extent to which a real gas depart from ideal behaviour may be depicted in terms of a function called compressibility factor, denoted by Z.
It is defined $Z = PV/RT$
The deviation from ideality may be shown by a plot of compressibility factor, Z against P.
For an ideal gas $Z = 1$. For real gases the deviation from ideal behaviour will be determined by the value of Z being greater or less than unity.

Effect of pressure : Fig 4 shows the compressibility factor Z, plotted against pressure for H_2, N_2 and CO_2 at constant temperature.

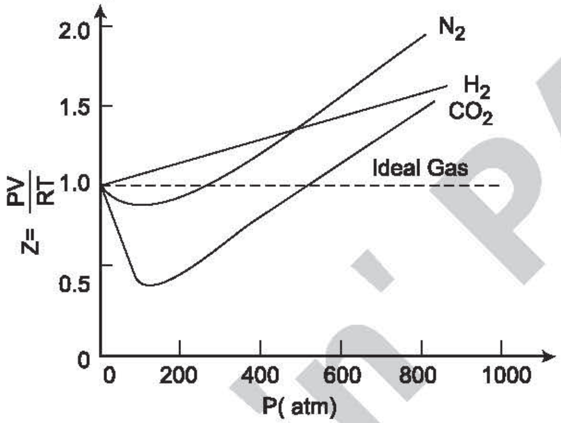


Fig. 4

At very low pressure for all these gases Z is approximately one. This indicates that all real gases exhibit ideal behaviour (upto 10 atm). For hydrogen curve lies above ideal gas curve at all pressure.

For nitrogen and carbon di-oxide, Z first decreases. It passes to a minimum then increases continuously with increase of pressure. For gas like CO_2 the dip in the curve is greatest as it is most easily liquified.

Effect of temperature : Fig 5 shows plot of Z against P at different temperature for N_2. It is clear from the plot that at low temperature deviation are more and at high temperature the gas tends to become ideal.

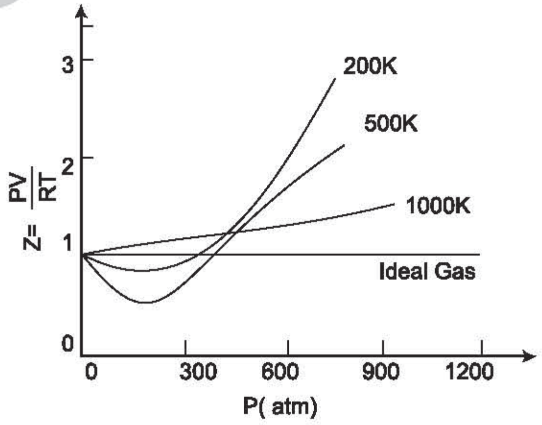


Fig. 5

(ii) Van der Wall's Equation of State

Van der Waal's 1873 studied the postulates of kinetic theory in detail and found that there are two faulty postulates.

(i) The molecules in a gas are point masses and possess no volume.

(ii) There are no intermolecular attractions in a gas. Van der Waal's was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation $PV = nRT$. His corrections are given below.

Volume correction : Volume of the gas in the available space for the movement of gas molecules. Volume V of an ideal gas is the same as the volume of the container. The dot molecule of ideal gas has zero-volume and the entire space in the container is available for their movement. But van der Waals assume that molecules of real gas are rigid spherical particles which posses a definite volume. The volume of real gas is, therefore ideal volume minus the volume occupied by gas molecules (Fig. 6). If b is the effective volume of molecules per mole of the gas then corrected volume should be $V - b = V_{\text{ideal}}$ For n moles $V_{\text{ideal}} = V - nb, b$ is also known as excluded volume.

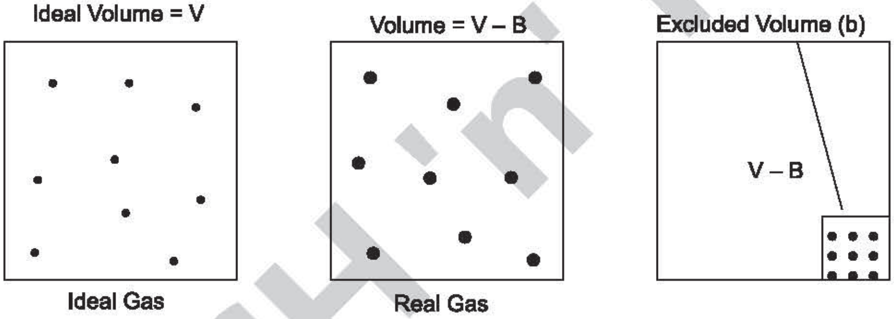


Fig. 6

Now let us consider two molecules of radius r colliding with each other (Fig. 7) Obviously they cannot approach each other closer than a

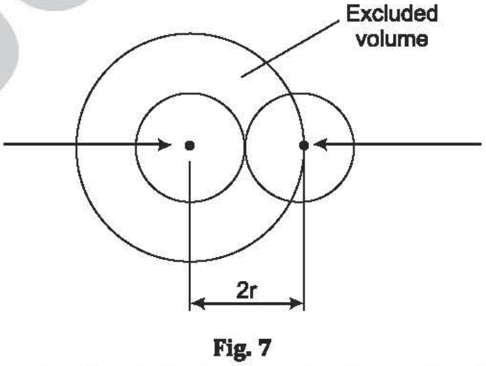


Fig. 7

Therefore, the space indicated by the dotted sphere having radius $2r$ will not be available to all other molecules of the gas. In other words the dotted space is excluded volume per pair of molecules. Thus,

$$\text{Excluded volume for two molecules} = 4/3\,\pi\,(2r)^3$$

$$= 8 \times 4/3\pi r^3$$

$$\text{Excluded volume per molecule} = \frac{1}{2} \times 8 \times \frac{4}{3} \pi r^3 = 4 \times 4/3 \pi r^3 = b$$

$$\text{For } n \text{ moles it is} = n \times 4 \times 4/3\pi r^3 = nb$$

Pressure correction : A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull (Fig. 8) due to unbalanced forces.

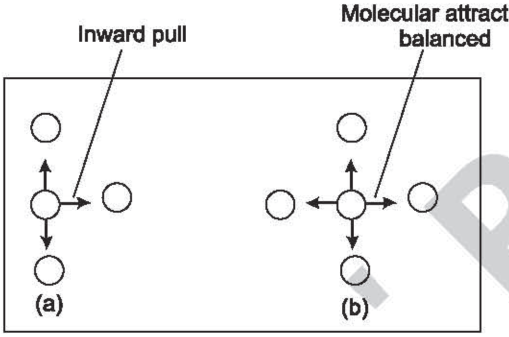


Fig. 8

Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas P, will be less than ideal pressure if the pressure P, is less than P_{ideal} by a quantity p, we have

$$P = P_{\text{ideal}} - p$$

Or $$P_{\text{ideal}} = p + p$$

The value of p is determined by the force of attraction between molecules (A) stricking the wall of the container and molecules (B) pulling them inward (Fig. 9).

The net force of attraction is, therefore, is proportional to the concentration of (A) type molecules and also of (B) type of molecules :

That is $p \alpha C_A \cdot C_B$

$$\alpha\, a \frac{n}{V} \times \frac{r}{V}$$

$$p = an^2/V^2$$

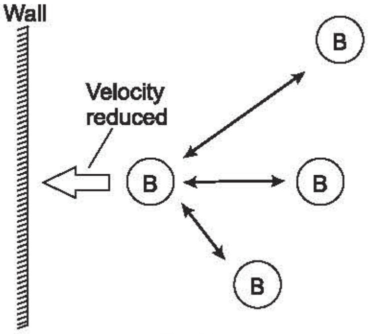


Fig. 9

n = total number of gas molecules in volume V.

Hencel ideal pressure

$$Pi = P + an^2/V^2$$

Substituting the value of corrected volume and pressure in the ideal gas equation $PV = nRT$, we have

$$(P + n^2 a/V^2)(V - nb) = nRT$$

This is equation for n moles for one mole.

We have $$(P + a/V^2)(V - b) = RT$$

van der Waal's equation can justify the deviations from ideal gas behaviour as given below :
The equation can be written as

$$PV - Pb + a/V - ab/V^2 =`P_iV_i$$

As ab/V^2 is very small quantity it can be neglected.

We get $$PV - Pb + a/V = P_iV_i$$

(i) At low pressure Pb is small as compared to a/v

We have $PV + a/V = P_iV_i$

Or $PV = P_iV_i - a/V$

That means observed product PV is less then P_iV_i, the product of pressure and volume if the gas were ideal.

(ii) At high pressure, the term Pb over weighs the term a/v

Then the equation can be written as

$$PV - Pb = P_iV_i$$

$$PV = P_iV_i + Pb$$

That is observed product PV is greater than P_iV_i

(iii) At high temperature as V is large, Pb and a/V will be negligibly small.

We have $PV = P_iV_i$

(iv) Exceptional behaviour of hydrogen. This is due to the very small mass of the hydrogen molecule due to which the forces of attraction between molecules are almost negligible. Therefore neglecting the term a/V

We have

$$PV = P_iV_i + P_b$$

Therefore in the case of hydrogen even at low pressure PV is greater than P_iV_i.

Q.2. What do you mean by PV isotherm of real gases? Give the isotherm of carbondioxides. Explain the continuity of state, the isotherms of van der Walls equation.

Ans.

PV Isotherms of Real Gases

- The connection between the concentrations of a solid and a fluid is known as an isotherm, and it is used to characterize states of no change in the sorption process.
- When pressure is raised at a constant temperature, volume decreases and vice versa. Isotherms are *P-V* curves that exist at a constant temperature.
- At high temperatures and low pressures, actual gases satisfy the ideal gas equation $PV = RT$.
- Due to interactions between gas molecules, a real gas does not behave like an ideal gas. Because the ideal gas law can only approximate the behaviour of a real gas, it is also known as a non-ideal gas.

Isotherm of Carbon Dioxide : Critical Phenomenon

Isotherm means pressure volume curve at constant temperature. For ideal gas the product of *PV* is constant and hence the isotherm would be rectangular hyperbola. (Fig 10). For most of the gases at normal temperature the shape of *P, V* curve is the same as it is for carbon dioxide gas.

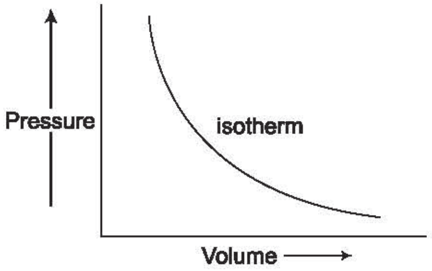


Fig. 10 : Pressure volume curve at a given temperature

Andrews in 1869 determined the isotherm of carbon dioxide at different temperatures. The isotherms of carbon dioxide determined by him at different temperature are shown in Fig. 11. Consider the first Isotherm at 13.1°C.

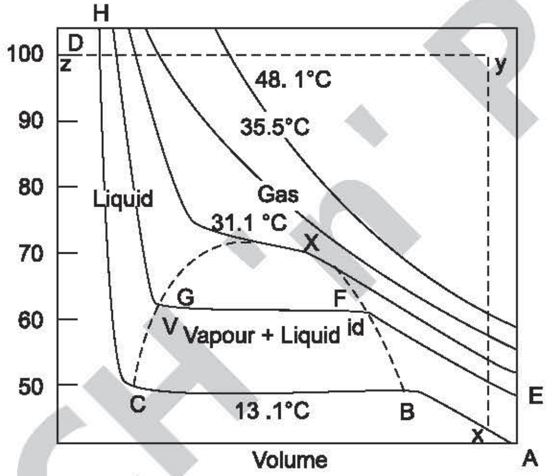


Fig. 11 : *P-V* isotherms of carbon dioxide

The point *A* represents carbon di-oxide in the gaseous state occupying a certain volume under a certain pressure. On increasing the pressure its volume diminishes as is indicated by the curve *AB*. At *B* liquification of gas commences and there after a rapid decrease in volume takes place at the same pressure as more and more of gas is converted into the liquid state. At *C*, the gas has been completely liquified. Now, as the liquid is only slightly compressible further increase of pressure produces only a very small decrease in volume. This is shown by a steep line *CD* which is almost vertical.

Thus along *AB*, carbon dioxide exists as gas; along *BC*, it exists partly as gas and partly as liquid while along *CD*, it exists entirely as liquid.

The curve *EFGH* at 21.5°C shows a similar behaviour except that now the liquification commences at higher pressure and the horizontal portion *FG*, representing decrease in volume, becomes smaller. At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1°C it reduces just to a point represented by *X*.

The curve passing through this point *X* marks the boundary between gaseous carbon dioxide and on the right and liquid carbon dioxide on the left.

Andrews noted that above 31.1°C there was no possibility of liquefaction of carbon dioxide how great the pressure is applied. At this temperature the gas is in critical state. The point *X* is then called the **critical point**. The isotherm passing through this point is called the **critical isotherm** and the temperature corresponding to this isotherm (31.1°C) is called **critical temperature.**

The critical phenomenon observed by Andrews in connection with carbon dioxide may be observed with any other gas. The pressure required to liquefy the gas at critical temperature is called the critical pressure and the volume occupied by one mole of the gas under these conditions is called **critical volume**.

Continuity of State

A careful examination of the isotherm plotted in fig. 8 shows that it is possible to convert liquid carbondioxide into gas and vice-versa, without any discontinuity that is without having at any time more than one phase present, on joining the end of the horizontal portion of the various isotherm, a bonding curve *CGXFB* represented by the dotted line is obtained. At the top lies the critical point *X*, with in the area of the boundary curve, both liquid and gaseous state can coexist but outside this area either liquid or gaseous state alone can exist. Because of this coexistence curve, it is possible to distinguish between the two states of matter, namely, gas and liquid. However in practice this is not always true because it is possible to convert matter from one state into another without any sharp discontinuity.

This can be done as shown in fig. 11 :

1. Increase the temperature of the gas keeping volume constant. The pressure rises along *xy*.
2. Having reached *y*, the pressure is kept constant and the gas is cooled; this decrease the volume along the line *yz*.

Thus we have passed from *x* to *z* without the gradual change as it occurs along the line *BC*, *i.e.*, condensation in the usual sense of the term did not occur. Point 2 could be said to represent a highly compressed gaseous state of the substance. Whether we refer to the state in the region of point *z* as liquid state or as highly compressed gaseous state depends purely upon which of the two view points happens to be convenient at the moment. Thus, in the absence of the surface of discontinuity, there is no way of distinguishing between liquid and gas.

Isotherm of van der Walls equation (Van der Waals Equation and the Critical Phenomena)

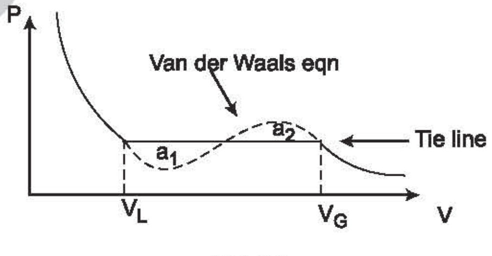


Fig. 12

The isotherms obtained by plotting the curve $PV = nRT$ are rectangular hyperbolas. Gases approximate to this isotherm at low pressures and high temperatures. The behavior of real gases, however, is better represented by the **Van der Waals' equation** as pointed out. The accurate measurements of the isotherms of gases have proved exceptionally important in the determination of interatomic forces. When the van der Waals' equation for one mole is suitably rearranged, we obtain a cubic equation in *V* as shown below :

$$V^3 - (b + RT/P)V^2 + (a/P)V - ab/P = 0 \qquad ...(1)$$

If one plots this equation graphically in the form of a $P - V$ isotherm, a curve of the type *ABCFDGE* (Fig. 13) is obtained. Such curves may be termed as van der Waals isotherms. This equation has three roots, *i.e.*, three values of *V* for any given value of *P* and *T*. All three roots may be real or one or two roots real and the others imaginary. When the roots are real and different three different values of *V* (for a given *P* and *T*) are shown in the points *B*, *F* and *G* in curve *I*. As *T* increases the three points get closer until they are identical, as in the critical isotherm, curve *II*. At higher temperatures the curve approximates a rectangular hyperbola, curve *III*, there bring one real root and two imaginary roots.

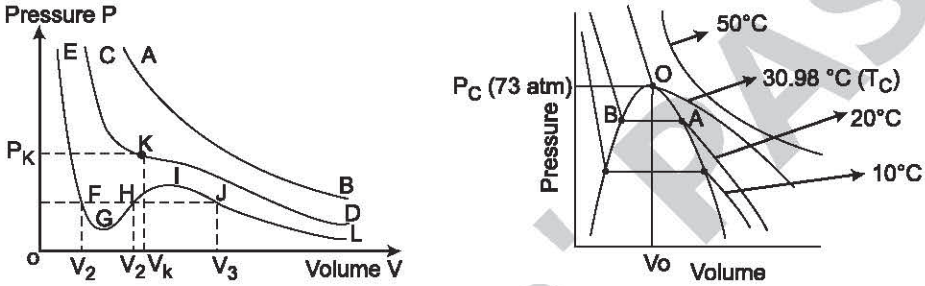


Fig. 13 : Isotherms for CO_2 according to van der Waals equation at different temperature

Andrew's experiments with carbon dioxide agree with the deduction from the van der Waals equation except for the shaped portion. Andrews obtained the horizontal portion representing a condensation of the gas, *i.e.*, the equilibrium between gas and liquid. Since three roots of the equation (1) are identical at the critical temperature, there is only one value of *V*, namely, the critical volume, V_c, which will satisfy this equation when the pressure and temperature have the critical values, P_c and T_c.

It is possible to express the critical constants in terms of the van der Waals constants in the following way :

A cubic equation in *V*, which has three identical roots, V_c, may be written in the form;

$$(v - V_c) = 0 \qquad ...(2)$$

Expanding this equation

$$V^3 - 3V^2V_c + 3V \cdot V_c^2 - V_c^3 = 0 \qquad ...(3)$$

Under the same condition's equations (1) becomes,

$$\mathbf{V^3 - (b + RT_c / P_c)V^2 + (a / P_c)V - ab / P_c = 0} \qquad ...(4)$$

Since equations (3) and (4) are simply different ways of writing the same equation, the co-efficient of V^3, V^2, V, etc. must, therefore, be the same in both the equations. Equating the co-efficient one obtains

$$3V_c = (b + RT_c / P_c); 3V_c^2 = (a / P_c); V_c^3 = (ab / P_c) \qquad ...(5)$$

From these equations, one can obtain the following values for P_c, V_c and T_c.

$$V_c = 3b; P_c = a / 27b^2; T_c = 8a / 27Rb$$

If the value of *a* and *b* are known, the critical constants may be calculated. Conversely, the equations may be arranged to obtain the expressions;

$$a = 27/64\,(R^2T_c^2 / P_c) \text{ and } b = RT_c / P_c$$

so that one can calculate a and b from the normal temperature and pressure. The critical volume, V_c has been eliminated from this expression as this is generally less accurately known than the values of P_c and T_c. By combining the equations (5) one may obtain the relation;

$$RT_c / P_c V_c = 8/3 = 2.67$$

Q.3. Discuss in brief the following :

(i) Reduced equation of state.

(ii) The law of corresponding state.

Ans.

(i) Reduced Equation of State

An equation which expresses the relation between pressure volume and temperature of a gas is called the equation of state or the characteristic equation. If we express the actual pressure, volume and temperature as fractions of the critical pressure, volume and temperature respectively, we get the reduced equation of state.

If the values of pressure, volume and temperature be expressed as fractions of the corresponding critical values, we get

$$P/P_c = \pi, \quad V/V_c = \Phi, \quad T/T_c = \theta$$

Where π, Φ and θ are termed the reduced pressure, reduced volume and reduced temperature respectively.

From above $P = \pi P_c,\ V = \Phi V_c$ and $T = \theta T_c$

If we replace P, V and T by $\pi P_c, \Phi V_c$ and T_c respectively in van der Waals equation

$$(P + a/V^2)(V - b) = RT$$

We get $\{\pi Pc + a/\Phi V_c)^2\}\{\mathrm{T}V_c - b\} = R\theta\, Tc$

Substituting the value of $V_c = 3b, P_c = a/27b^2$

And $T_c = 8a/27Rb$ we get

$$\left\{\pi \frac{a}{27b2} + a/9\Phi^2 b^2\right\}\{3\Phi b - b\} = R\theta \frac{8a}{27Rb}$$

Dividing the above equation throughout by $a/27b$

We get $\{\pi + 3/\Phi^2\}\{3\Phi - 1\} = 8\theta$

This equation is known as van der Waals reduced equation of state.

(ii) The Law of Corresponding States

Van der Waals reduced equation of state is given by

$$\{\pi + 3/\Phi^2\}\{3\Phi - 1\} = 8\theta \qquad ...(1)$$

In this equation the quantities $a, b\ P_c, V_c$ and T_c which are characteristic of a given gas have cancelled out, thus making it applicable to all substances in the liquid or gaseous state, irrespective of their specific nature. From equation (1) it is clear that when two substances have the same reduced temperature and pressure they will have the same reduced volume. This is known as the law of corresponding states. When two or more substances are at the same reduced temperature and pressure, they are said to be in corresponding state.

In actual practice, the above reduced equation of state is not directly used. One makes use of graphs between compressibility factor z and reduced pressure at different reduced temperature. The same graphs are applicable to all gases. This can be seen from the following considerations.

Since $$Z = PV/RT = \pi P_c \cdot \Phi V_c / R\theta T_c$$

If we put the values of P_c, V_c and T_c

We get $$Z = \frac{3\pi\Phi}{8\theta} \quad ...(2)$$

According to law of corresponding states, if two gases have the same reduced temperature and reduced pressure they will have the same reduced volume. The right hand side of the equation (2) is independent of the nature of gas and Z is same for all gases.

In practice this means that the properties of liquids should be determined at the same reduced temperature because pressure has very slight effect on them. Since it is found that boiling points of liquids are approximately (2/3)rd of the critical temperature, it follows that liquids are at their boiling points approximately in corresponding states. Therefore, in studies the relation between the physical properties of liquids and chemical constitutions, the physical properties may be conveniently determined at the boiling points of liquids.

Q.4. (i) Write a note on mean free path.

(ii) Describe maxwell's law of distribution of velocities among the velocities.

Ans.

Mean Free Path

A very important quantity in kinetic theory of gases is the mean free path. At a given temperature, a molecule travels in straight line before collision with another molecule.

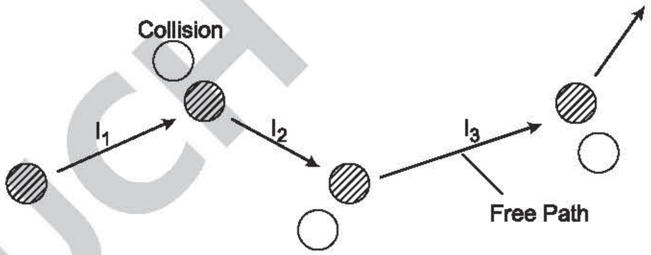


Fig. 14 : Mean free path

The distance travelled by the molecule before collision is termed free path. The mean distance travelled by a gas molecule between two successive collisions is called the **mean free path.** It is denoted by λ. If l_1, l_2, l_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{l_1 + l_2 + l_3 \; .... \; l_n}{n} \quad ...(1)$$

Where n is number of molecules with which the molecule collides. Evidently, the molecular collisions will be less at a lower pressure or lower density and longer will be the mean free path. Mean free path is also related with viscosity of the gas.

$$\lambda = \eta\sqrt{3/P_d}$$

where p = pressure of the gas

η = coefficient of viscosity of the gas

d = density of the gas

From the above equation it is clear that by the determination of viscosity mean per path can be calculated. At NTP the mean free path for hydrogen is 1.78×10^{-5} cm and for oxygen 1.0×10^{-5} cm.

Effect of temperature on mean free path :

The ideal gas equation is $PV = nRT$ ...(2)

Where n is number of moles given by

$$n = \text{No. of molecules/Avogadro's number} = N / N_0$$

Substituting the value of n in equation (2)

$$PV = N / N_0 \times RT$$

or $$N / V = (PN_0) / RT$$

At constant pressure $$N \propto \frac{1}{r} \qquad ...(3)$$

The mean free path is given by

λ = Distance Travelled by the molecule per second/Number of collisions per cc.

$$= v / \sqrt{\pi\sigma^2 vN} \qquad ...(4)$$

Combining equation (3) and equation (4) $\pi \propto T$

thus mean free path is directly porportional to the absolute temperature.

Effect of Pressure on mean free path : We know that the pressure of a gas at certain temperature is directly proportional to the number of molecules cc. that is,

$$P \propto N$$

and mean free path is $$\lambda = 1 / \sqrt{2\pi\sigma^2 N}$$

Hence we get $$\lambda \propto 1 / P$$

Thus mean free path is inversely proportional to the pressure of a gas at constant temperature.

(ii) Maxwell's law of distribution of velocity among the Molecules

The molecules of a gas are in random motion. There is a continuous change in the magnitude and direction of their velocities (speeds) due to random motion and collisions between the molecules. **Maxwell** analysed the distribution of velocities by the statistical method.

Maxwell's law : According to this law, the number of molecules (dn) possessing velocities between c and $c + dc$ is given by

$$dn = 4\pi n a^3 e^{-bc^2} c^2 dc \qquad ...(1)$$

Where n is the number of molecules per unit volume and $a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}}$

Relation (1) is called Maxwell's law of distribution of velocities.

Let $bc^2 = x^2$, differentiating $2bc\,dc = 2x\,dx$ or $dc = x\,dx / bc$.

Also $a = \sqrt{\frac{b}{\pi}}$. Thus $a^3 = \left(\frac{b}{\pi}\right)^{3/2}$ Also $c = \sqrt{b}x$.

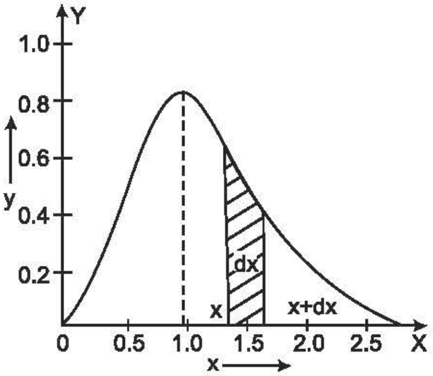


Fig. 15

Substituting the above terms in equation (1) we get

$$\frac{dn}{n} = 4\pi \left(\frac{b}{\pi}\right)^{3/2} e^{-x^2} \frac{x}{bc} dx$$

Simplifying the above equation $\frac{dn}{n} = 4\pi^{-1/2} e.$

Plotting Maxwell speed distribution function y, versus x ($y = f(v) = dn/n$ and x the molecular speed) we get the graph as shown.

1. The shaded region between x and $x + dx$ gives the total number of molecules (dn/n) whose velocities lie between c and $c + dc$.
2. The area under the graph gives the total number of molecules n with velocities between zero and infinity.
3. The co-ordinate y corresponding to any value of x gives the number of molecules having velocity represented by x.
4. dn/n is maximum at $x = 1$ which represents the most probable velocity.

●

UNIT-V

Liquid State

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Write three properties of liquids.

Ans. 1. Density, 2. Compressibility, 3. Diffusion.

Q.2. Write the factors that affect evaporation.

Ans. 1. Surface area, 2. Nature of the liquid, 3. Temperature, 4. Flow of air current over the surface of liquid.

Q.3. Write the intermolecular forces in liquids.

Ans. 1. Dipole-dipole interaction, 2. Ion-dipole interaction, 3. Dipole-induced dipole interaction, 4. Instantaneous dipoles-induced dipole interaction.

Q.4. What is the condensed state of matter.

Ans. The state of matter in which molecules approach so close that the attractive forces between them keep the molecules together is known as condensed state of matter.

Q.5. Write the two substances showing liquid crystal character.

Ans. 1. *p*-Azoxyanisole, 2. Diethylbenzidine

Q.6. Write the types of liquid crystals.

Ans. 1. Smectic liquid crystals, 2. Nemetic liquid crystals, 3. Cholesteric liquid crystals

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. Write a short note on liquids.

Ans.

Liquid

Liquids include all the states of matter similar to water. As compared to solids, the particles in a liquid are less tightly packed. The atoms in a liquid can move freely within a limited space. The properties of atoms in liquids are as follows :

- Atoms have considerable space between each other for movement.
- They do not have a definite position inside the arrangement and can travel anywhere inside the liquid.
- In liquids the kinetic energy of atoms is much greater than solids but less than gases.

Due to the aforementioned behaviour of the particles, liquids have the following properties :

- Liquids do not have a definite shape. They can change the shape according to the shape of the solid they are stored in. For instance, water changes its shape from a bottle shape to a glass shape when poured out of the water bottle into a drinking glass.
- The intermolecular force of attraction between two atoms is moderate. For this reason, even liquids are hard to compress.

- Like solids, they also have constant mass and volume.
- The fluidity of liquids is moderate, they can easily travel.
- The density of liquids is less than solids but more than gases.

Q.2. Give the comperison of chracteristics of gases, liquids and solids and the microscopic explanation for the behaviour.

Ans. Comparison of Characteristics of Gases, Liquids and Solids and the Microscopic Explanation for the Behavior :

Gas	Liquid	Solid
Assumes the shape and volume of its container particles can move past one another.	Assumes the shape of the part of the container which it occupies particles can move/slide past one another.	Retains a fixed volume and shape rigid-particles locked into place.
Compressible lots of free space between particles.	Not easily compressible little free space between particles.	Not easily compressible little free space between particles.
Flows easily particles can move past one another.	Flows easily particles can move/slide past one another.	Does not flow easily rigid-particles cannot move/slide past one another.

Liquids, like gases, are characterized by the absence of a long-order range, which is present in the crystalline materials. However, they do have a medium-order range that is produced due to the chemical bonds and their interactions.

To study the structure of liquids, it is also important to understand and study macroscopic properties of matter, which includes interconversion of the 3 states namely, gases, liquid, and solids.

The structure of liquids can be studied computationally by using quantum mechanics and also by suing techniques like Monte-Carlo Simulation, Molecular dynamics, diffraction methods, and NMR.

Q.3. Give the structure of liquid crystals.

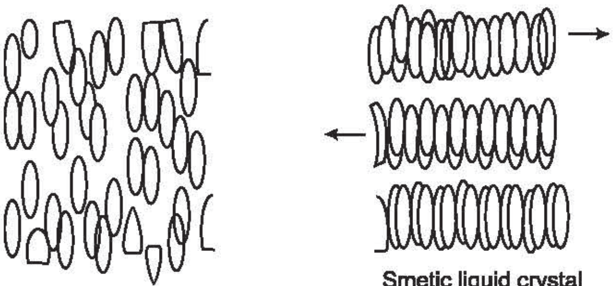
Ans.

Structure of Liquid Crystals

In a liquid the moleucules have random arrangement and they are able to move fast each other. In a solid crystal the molecules have an ordered arrangement and are in fixed positions. In a liquid crystal, however, molecules are arranged parallel to each other and can flow like a liquid. Thus liquid crystals have the fluidity of a liquid and optical properties of solid crystals.

Accordingly to their molecular arrangement, the liquid crystals are classified into three types :

1. **Nematic liquid crystals :** In nematic liquid crystals molecules are parallel to each other like soda straws but they are free to slide or roll individually.
2. **Smetic liquid crystals :** The molecules in this type of liquid crystals are also parallel but these are arranged in layers. These layers can slide past each other (Fig 1).



Nematic liquid crystal

Smetic liquid crystal

Fig. 1

3. **Cholesteric liquid crystals :** As in nematic crystals in this type liquid crystals the molecules are parallel but arranged in layers. The molecules in successive layers are slightly rotated with respect to the layers above and below so as to form spiral structure.

Q.4. Write two applications of liquid crystals.

Ans.

Application of liquid crystals

On account of their remarkable optical and electrical properties, liquid crystal found several practical applications. Some of these are given below.

Number display : When a thin layer of nematic liquid crystal is placed between two electrodes and an electrical field is applied, the polar molecules are pulled out of alignment. This cause the crystal to be opaque. Transparency returns when electrical signal is removed. This property is used in the number displays of digital watches, calculators, and other instruments.

Monitoring body temperature : Like the solid crystals, liquid crystals can diffract light. Only one of the wavelengths of the white light is refracted by the crystal which appears coloured. As the temperature changes the distance between the layers of molecules also changes. Therefore the colours of the reflected light changes correspondingly. These colesteric liquid crystal undergoes a series of colour changes with temperature. These crystals are used in indicator tapes to monitor body temperature or to spot areas of overheating in mechanical systems.

Q.5. Tabulate the qualitative description of molecular structure of solids, liquids and gases.

Ans. Qualitative description of molecular structure of solids, liquids and gases :

	Solids	**Liquids**	**Gases**
Arrangement	The particles in a solid are arranged in a fixed pattern.	The particles in a liquid are not arranged in any fixed pattern.	The particles in a gas are arranged in a random manner.
Separation	The particles of a solid are very close to each other.	The particles in a liquid are close to each other.	The particles of a gas are further apart from each other.
Motion	The solid particles can only vibrate in their fixed (mean) positions.	The liquid particles can slide past over each other.	The gas particles are free to move everywhere rapidly.

In a solid :

- The molecules are arranged in a three dimensional structure.
- Each molecule vibrates about a fixed mean position.
- When a solid is heated its molecules gain kinetic energy and vibrate more.
- If sufficient heat is provided, then enough energy may be given to the molecules so that they weaken their bonds from the neighbouring molecules in the lattice structure. When this happens, the solid melts or sublimes.

In a liquid :

- The molecules are in contact with each other and also move around freely.

- The forces of attraction between the liquid molecules are weak compared to solids, so they can slide past over each other. Hence they can flow and do not have a fixed shape.
- The forces of attraction are strong enough to stop the molecules from leaving the liquid surface.
- When a liquid is heated, some of the molecules gain enough kinetic energy to break away from the other molecules and leave the liquid surface and change to a gaseous form.

In a gas :

- The forces of attraction between gas molecules is negligible. So a gas can flow and has no fixed shape.
- The molecules move about freely in the container, colliding with each other and with the walls of the container.
- When a gas is heated, its molecules gain kinetic energy and move more rapidly and collide more frequently, thus exerting gas pressure.

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. What are intermolecular forces? Discuss in detail.

Ans.

Intermolecular Forces

The forces existing between the molecules of a substance are called intermolecular forces, while those existing within each molecule of a substance are referred to as intramolecular forces.

The intermolecular forces are electrostatic in nature and are much weaker than chemical forces. They exist in all the states of matter and play an important role in deciding several structural features and physical properties of matrer. An idea of the strength of intermolecular forces operating among the molecules of a substance can be had from the boiling point of the substance. *Higher the boiling point, greater is the magnitude of intermolecular forces.* Similarly, the melting points of substances increase with increase in the strength of intermolecular forces.

The intermolecular forces come into existence due to the following types of interactions :

(i) Dipole-dipole interactions
(ii) Dipole-induced dipole interactions
(iii) Ion-dipole interactions
(iv) Ion-induced dipole interactions
(v) Dispersion forces
(vi) Hydrogen bonding.

The intermolecular forces arising on account of dipole-dipole interactions, dipole-induced dipole interactions and dispersion forces are also referred to as *Van der Waals forces.*

A brief discussion of the different types of interactions is given below.

1. **Dipole-Dipole Interactions (Keesom Forces) :** The forces which come into existence by dipole-dipole interactions are called Keesom forces. When polar molecules (molecules having permanent dipole moment) are brought closer, they orient themselves in such a way that the positive end of one dipole is opposite to the negative end of some other dipole or vice-versa. Thus, the two dipoles attract each other by an

electrostatic force (Fig. 2). The dipole-dipole interactions are more pronounced at low or moderate temperatures.

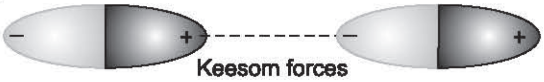


Fig. 2 : Dipole-dipole interaction

2. **Dipole-Induced Dipole Interactions (Debye Forces) :** Sometimes a polar molecule (having a permanent dipole moment) distorts a normal non-polar molecule and induces a dipole moment in it. The forces developed due to interaction between a dipole and an induced dipole are called **Debye forces**.

   Debye forces come into existence when a polar molecule is brought closer to a non-polar molecule. The positive end of the polar molecule attracts the mobile electrons of the non-polar molecule, distorts it and changes it into an induced dipole (Fig. 3). The positive end of the permanent dipole molecule can now attract the displaced electron cloud of the induced dipole and the two are held together by an electrostatic attraction.

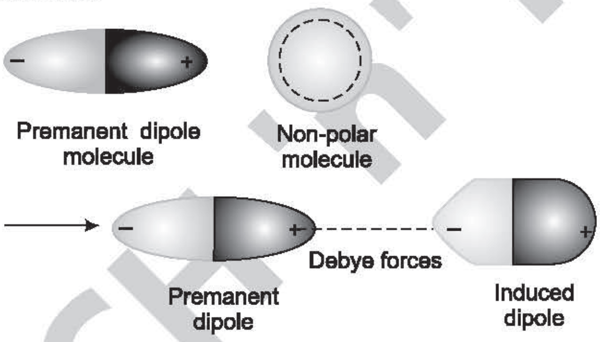


Fig. 3 : Dipole-induced dipole interaction

   Debye forces are not affected by temperature. However, they depend upon the distance between dipole and induced dipole.

3. **Ion-Dipole Interactions :** The ion-dipole interactions involve the attraction between an ion (either a cation or an anion) and a polar molecule. The strength of ion-dipole interaction depends on the charge and size of the ion and also on the magnitude of dipole moment and size of the polar molecule. Since, the charge density on cations is higher as compared to that on anions, cation attracts a dipole more strongly than an anion having the same charge but bigger size.

   The hydration of ions is due to this type of interactions. When an ionic compound is dissolved in water, the ions attract water molecules which have a large dipole moment and get hydrated. Thus, water molecules act as a dielectric to keep the ions apart. The non-polar liquids such as carbon tetrachloride act as a poor solvent for ionic compounds because they are unable to participate in ion dipole interaction.

4. **Ion-Induced Dipole Interactions :** Sometimes, an ion distorts a normal non-polar molecule and induces a dipole moment in it and attractive forces are developed between the ion and the induced dipole. The magnitude of the dipole moment induced depends not only on the charge present on the ion but also on the polarisability of the non-polar molecule.

5. **Dispersion Forces :** Some sort of attractive forces also exist in between neutral molecules and atoms inspite of the fact that they are not polar in nature. The non-polar molecules like H_2, O_2, Cl_2, I_2, etc., and monoatomic noble gases such as He, Ne, Ar, Xe, etc., also develop this type of forces. Such forces come into existence due ton in **stantaneous dipoles** created in these non-polar molecules or atoms and are called **dispersion forces**.

   The existence of dispersion forces in such molecules is due to the development of an instantaneous or temporary dipole moment in them. Atoms and molecules are electrically symmetrical and as such do not possess any dipole moment. However, any slight relative displacement of the nuclei or the electrons may develop an instantaneous or temporary dipole moment in them and for a moment they may act as dipoles . Such displacements are very common and constantly occur in atoms and molecules. These displacements are temporary and random. Therefore the molecule as a whole has no measurable dipole moment. The formation and decay of a temporary dipole is shown in Fig. 4.

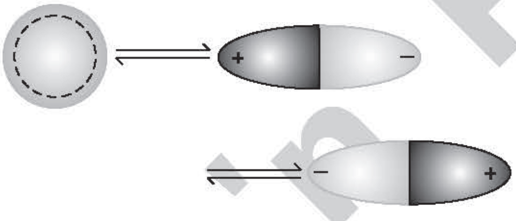


Fig. 4 : Instantaneous formation and decay of a dipole in a gas atom

   At the moment the molecule develops a temporary dipole moment, it can polarise a neighbouring non-polar molecule and may change it into an induced dipole. The two can thus be held together by electrostatic forces called **dispersion forces** or **London forces.** These forces are very weak because the atoms and molecules are in ceaselessly rapid motion and are constantly departing from the sites of temporary dipoles.

6. **Hydrogen Bonding :** When a hydrogen atom is bonded to a highly electronegative atom through a covalent bond, the electronegative atom tries to pull the shared electrons towards its own side resulting in the development of a large partial negative charge on the electronegative atom and a corresponding partial positive charge on the hydrogen atom. Now, the positively charged hydrogen atom of one molecule may attract the negatively charged atom of some other molecule and the two molecules can be linked together through a weak force of attraction. This weak force of attraction is known as the **hydrogen bond** or **hydrogen bonding**. It is represented by a dotted line (---). For example, in the molecule HF, F atom is highly electronegative and acquires a partial negative charge due to pulling of the shared pair. Therefore in HF, H atom possesses a partial positive charge and the molecule of HF can be represented as $H^{\delta+}—F^{\delta-}$. Due to the presence of partial positive and negative charges, several molecules of HF link together through hydrogen bonds as shown below.

$$\ldots H^{\delta+}—F^{\delta-}\underset{\substack{\uparrow\\ \text{hydrogen}\\ \text{bond}}}{\ldots}H^{\delta+}—F^{\delta-}\ldots H^{\delta+}—F^{\delta-}\ldots H^{\delta+}—F^{\delta-}\ldots H^{\delta+}—F^{\delta-}$$

Due to the presence of hydrogen bonding, hydrogen fluoride exists as a cluster of several HF molecules and is represented as $(HF)_n$. Hydrogen bonding may be defined as follows.

The weak attractive force which binds the partially positively charged hydrogen atom of one molecule, with the partially negatively charged atom of some other molecule of similar or different type, or with some other negative centre of the same molecule; is referred to as hydrogen bond or hydrogen bonding.

Hydrogen bond is much weaker as compared to a covalent bond. The bond energy of a hydrogen bond lies between 3.5-40 kJ mol^{-1} (the bond energy of a covalent bond is usually of the order of 400 kJ mol^{-1}). The bond length of a hydrogen bond is greater than that of a covalent bond. For example in $(HF)_n$, the bond length of H - - - - F (hydrogen) bond is 255 pm while that of H—F (covalent) bond is only 92 pm.

Conditions for Hydrogen Bonding

Hydrogen bonding is formed on account of dipole-dipole interaction between the molecules. Therefore, following conditions favour the formation of hydrogen bonding :

1. **High electronegativity of the atom bonded to hydrogen :** Hydrogen atom should be bonded to a highly electronegative atom such as F, O, or N. Higher the electronegativity of the atom bonded to hydrogen, greater is the strength of hydrogen bond. Since, the electronegativities of F, O and N follow the order F > O > N, the strength of hydrogen bond decreases in the order.

   H-----F > H --- ---O > H ---N
2. **Small size of the electronegative atom :** For an effective hydrogen bonding, it is necessary that the size of the electronegative atom be small. If the size of the electronegative atom is large, its attraction on the bonded pair will be less. Consequently, less polarity will be developed in the molecule and the resulting hydrogen bond will be weaker. For example, N and Cl possess the same value of electronegativity (3.0), yet NH_3 shows hydrogen bonding while HCl does not due to larger size of Cl atom.

Q.2. Describe the structure and characteristic properties of liquids. Also give the structural differences between solid, liquid and gases.

Ans.

Structure of Liquids

In a liquid, the molecules are not as rigidly fixed an in solid. They have some freedom of motion which, however, is much less than that in a gas. Liquids resemble solids in being compact, incompressible and in having a definite volume. These properties are indicative of a regular structure in liquids similar to that in solids.

From X-ray diffraction technique, it has been found that the resemblance of liquid state with solid state is valid with in a small range; i.e. within only small distance from a given molecule. In other words the regularly ordered structure which exists in crystalline solids is of short range in liquids. It means it exists in only within a short distance from any given molecule. A solid possesses short range as well as long range order since the ordered structure extends regularly throughout the whole crystal.

Now it should be clear to you that

1. A gas consists of molecules separated wide apart in empty space. The molecules are free to move about throughout the container.

2. A liquid has molecule touching each other. However, the intermolecular space, permit the movement of molecule throughout the liquid.
3. A solid has molecules, atoms or ions arranged in a certain order in fixed position in the crystal lattice. The particles in a solid are not free to move about but vibrate in their fixed position.

Properties of Liquids

The observed macroscopic properties of liquids can easily be understood on the basis of **kinetic molecular model** of liquids. The important features of this model are as follows :

1. Liquids are composed of molecules.
2. There are appreciable forces of attraction between the molecules of a liquid.
3. The molecules are in a state of constant rapid motion in a liquid.
4. The average kinetic energy of the molecules in a given sample of liquid is proportional to the absolute temperature.

Some of the important properties of liquids are given below.

1. **Volume :** Liquids possess a definite volume which is independent of the shape or size of the container. Whatever be the shape or size of the container, volume of a liquid remains constant at a constant temperature. A liquid always remains confined to the lower part of the container and does not spread in the entire space available to it as the gases do. This is because in liquids, the molecules are comparatively closer together and are bound by stronger forces. Therefore, they are unable to occupy the entire space available to them.

   However, the shape of the liquids is not fixed. They acquire the shape of the container in which they are filled as shown in Fig. 5.

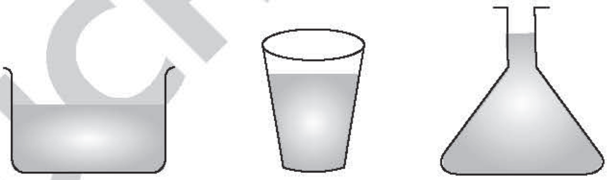


Fig. 5 : Liquids acquire the shape of container.

2. **Density :** In a liquid, the molecules are more closely packed as compared to the gases. Therefore, the densities of liquids are much higher than those of gases under similar conditions. For example, the density of water at 100°C and 1 atm pressure is 0.958 g/cm ^{3} while that of water vapour is 0.000588 g/cm^3 at the same temperature and pressure.
3. **Compressibility :** Due to comparatively closer packing of molecules, liquids are much less compressible as compared to gases. For example, the volume of liquid water decreases by 0.0045% only when pressure on it is increased from 1 atm to 2 atm. Under similar conditions, the volume of an ideal gas decreases by 50%.
4. **Diffusion :** Liquids also possess the property of diffusion but their rates of diffusion are much less as compared to those of gases. This is because, in a liquid, the molecules are more closely packed and the inter-molecular space (free space) available for their movement is much smaller as compared to gases. Moreover, the molecules in a liquid are held together by stronger cohesive forces. This also prevents the molecules from

moving faster. Due to these factors, the rate of diffusion of a liquid is much less than that of a gas.

5. **Evaporation :** When a liquid is placed in an open vessel, it gradually changes into vapour and disappears after sometime. *This process of gradual change of a liquid into vapour at room temperature is called evaporation.* Evaporation is a spontaneous process and takes place at all temperatures. The rate of evaporation increases with increase in temperature.

   The process of evaporation can be understood on the basis of kinetic molecular model of the liquids. A liquid is composed of molecules which are in a constant rapid motion and possess kinetic energy. These molecules attract each other by appreciable force. The distribution of velocity and hence of kinetic energy in a liquid is almost similar to that found in gases. At a particular temperature all molecules do not possess the same kinetic energy inspite of the fact that the temperature of the liquid is uniform and the average kinetic energy of the molecules is constant. Therefore, at room temperature (and at all other temperatures also) a fraction of molecules possesses sufficient kinetic energy to overcome the cohesive forces between the molecules of a liquid. These molecules are more energetic as compared to other molecules. When such energetic molecules reach the surface of the liquid, they overcome the cohesive forces of the neighbouring molecules and escape into the space above the liquid surface. The molecules thus escaped constitute the vapour of the liquid. After the escape of these molecules, the remaining liquid acquires the same distribution of kinetic energy (if the temperature is maintained constant) and again the most energetic fraction escapes in the same way. The process continues till there is no liquid left in the vessel.

6. **Heat of Vaporisation :** The heat of vaporisation of a liquid at a particular temperature is defined as the amount of heat required to evaporate the given liquid at that temperature.

Molar heat of vaporisation ($\Delta v_{vap} H$) is defined as the amount of heat required to evaporate one mole of a liquid at a constant temperature.

Comparison between Solids, Liquids and Gases

The solid, liquid and gas are the three forms of matter. These forms of matter differ considerably in their properties. The main cause of difference in their behaviour is the difference in the intermolecular distance and the magnitude of intermolecular forces between their molecules. A comparison of the properties of these three forms of matter is given in following Table .

S. No.	Property	Solids	Liquids	Gases
1.	**Arrangement of constituent particles**	The constituent particles (atoms, molecules or ions) are closely packed and occupy fixed positions in the lattice. Thus, solids possess long range order.	The constituent particles are less orderly packed. Thus liquids possess short range order.	There is no definite arrangement of constituent particles and they are widely separated from one another.

2.	**Inter-particle distances**	Inter-particle distances are fixed and are very small.	Inter-particle distances are greater than those in solids and are slightly variable.	The inter-particle distances are quite large as compared to those in solids and liquids.
3.	**Movement of particles**	The constituent particles can only vibrate about a fixed point.	The particles are free to move in such a way that they always remain in contact with one another. Infact they are free to move within the boundary of the liquid.	The particles are free to move in all directions. They can undergo translational, rotational as well as vibrational motions.
4.	**Shape**	Since the constituent particles are fixed at lattice points and have well defined arrangement, solids have definite shape.	Due to the absence of fixed positions of constituent particles, liqudis have no definite shape and acquire the shape of the container in which they are filled.	Due to the free movement of constituent particles in all directions, the gases have no definite shape.
5.	**Volume**	Due to the fixing of constituent particles at definite lattice points, the solids have fixed volume at a given temperature.	Since the constituent particles always remain in contact with one another, the liquids have a fixed volume at a given temperature.	Since particles are free to move in any direction, gases have no definite volume. A gas can fill uniformly any volume available to it.
6.	**Density**	Due to the close packing of constituent particles, solids have high density.	The densites of liquids are usually lower than those of solids.	Due to the large separation between the constituent particles, gases have low densities.
7.	**Compressibility**	Due to the close packing of particles solids possess very low compressibility and can be compressed only under very high pressures.	The liquids are more compressible as compared to solids.	Due to the large spaces between the constituent particles gases can be compressed to a great extent.
8.	**Diffusion**	Due to the lack of translational motion of the constituent particles, solids have practically no tendency to diffuse.	Since the constituent particles are free to move within the boundary of the liquid, the liquids have a tendency to diffuse although their rates of diffusion are much less than those of gases.	Due to the free movement of constituent particles, gases possess a great tendency to diffuse.

Q.3. What are liquid crystals? Give their types, characteristics and applications.

Ans.

Liquid Crystals

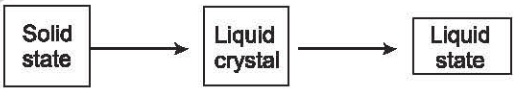
There are certain solids which on heating undergo two sharp phase changes one after the other. They first fuse sharply yielding turbid liquids and again equally sharply at higher temperature yielding clear liquids. These changes get reversed on cooling at the same temperature. The turbid liquid show anisotropy i.e. they have different physical properties from different directions. Anisotropy is particularly seen in the optical behaviour of liquids. In an anisotropic substance, the physical property are different in different direction. On the other hand true liquids are isotropic same physical properties in different directions. As anisotropic properties are associated with crystalline state, the turbid liquids are known as liquid crystals.

This liquid crystal term, however, is not satisfactory since the substances in this state do not have properties of crystalline state. Actually, they are more like liquids in having properties like mobility, surface tension, viscosity etc. Amongst other names that have been suggested are crystalline liquids and anisotropic liquids, but these are also not satisfactory. The term mesomorphic state (meaning intermediate form) probably fits best. But, the older term liquid crystal continues to be used even in the present day literature.

Substances which show the above behaviour are usually some long chain organic molecules either terminating in groups such as —OR, —COOR or having groups like —C═N—, —N═NO—, —C═C— in the middle. The first solid showing this peculiar property was discovered in 1888 was cholesteryl benzoate $C_6H_5COOC_{27}H_{45}$. It fuses sharply at 145°C to form turbid liquid and on further heating changes into clear liquid at 178°C. If we cool, the above changes are reversed i.e., the clear liquid when cooled first changes into turbid state at 178°C and then into the solid state at 145°C.

Later on, *p*-azoxyanisole and p-azoxyphenetone were found to exhibit the same properties. In 1991 **P.G. De Genees**, a French physicist got the Nobel Prize in Physics for contribution to liquid crystals and polymers.

$$\underset{\text{solid}}{\text{p-cholesteryl benzoate (pcb)}} \xrightleftharpoons{145^\circ\text{C}} \underset{\substack{\text{liquid}\\\text{crystal}}}{\text{p.c.b}} \xrightleftharpoons{178^\circ\text{C}} \underset{\text{liquid}}{\text{p.c.b}}$$



One such substance that forms liquid crystal is p-ozoxyanisole (Fig. 6) :

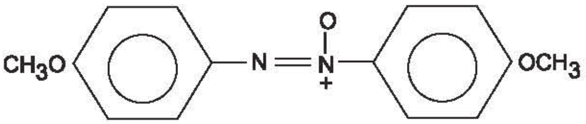


Fig. 6 : p-Ozosyanisole

Characteristics of Liquid Crystal : Liquid crystal materials generally have several common characteristics. Among these are a rod-like molecular structure, rigidness of the long axis, and strong dipoles and/or easily polarizable substituents.

The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state. The average alignment of the molecules for each phase in the following diagram.

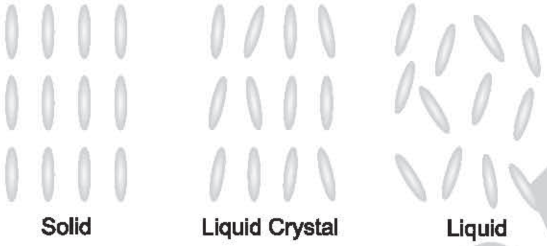
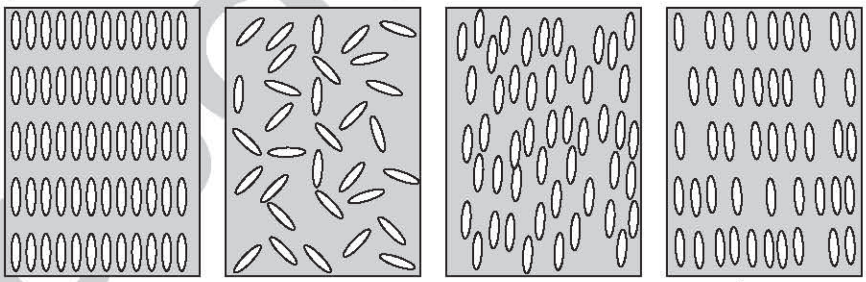


Fig. 7

Classification of Liquid Crystals

Liquid crystals are classified in many ways, molecules within the mesophases (mesogens) can be calamitic (rod-like), discotic (disc-like), amphiphilic, nonamphiphilic, metal containing, non-metal containing and low molecular weight or polymeric. Liquid crystals either show thermotropic behaviour or lyotropic behaviour. Thermotropic behaviour means the compounds are liquid crystalline within a defined temperature range, below this range compounds are crystalline and above it compounds are isotropic liquids. Thermotropic liquid crystalline compounds also require no solvent. Lyotropic liquid crystals are dependent on solvents, where solvent concentration affects aggregation and.

Liquid Crystal Behaviour



Solid Phase: orientation and periodicity

Liquid Phase: no orientation or periodicity

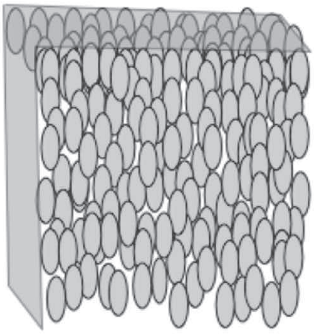
Nematic Phase: Orientation, no Periodicity

Smectic Phase: Orientation, With Some Periodicity

Fig. 8

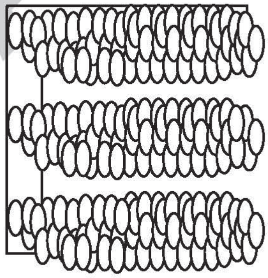
There are many classes and sub-classes of liquid crystals, but for the purposes we will divide them into the two types :

Nematic : In a nematic phase (the term means "thread-like") the molecules are aligned in the same direction but are free to drift around randomly, very much as in an ordinary liquid. Owing to their polarity, the alignment of the rod-like molecules can be controlled by applying an electric field; this is the physical basis for liquid crystal displays and certain other electro-optic devices.



Nematic

Fig. 9



Smectic
Fig. 10

Smectic : In smectic ("soap-like") phases the molecules are arranged in layers, with the long molecular axes approximately perpendicular to the laminar planes. The only long-range order extends along this axis; with the result that individual layers can slip over each other (hence the "soap-like" nature) in a manner similar to that observed in graphite. Within a layer there is a certain amount of short-range order. There are a large number of sub-categories of smectic phases which we will not go into here. Smectic liquid crystal has been found to have fast electro-optical response time and because of this is used, along with nematic liquid crystal, in producing liquid crystal display (LCD) screens.

Applications of Liquid Crystals

1. Research on optical & electrical properties of these unique compounds attracted very much by scientific and industrial community. Later, research at a number of industries, universities and government laboratories began to focus on their applications, which exploited the electro-magneto-optic characteristics and photoelectric properties of nematic and cholesteric type liquid crystals.
2. Cholesteric liquid crystal substances, when applied to the surface of the skin, have been used to locate veins, arteries, infections, tumors and the fetal placenta which are warmer than the surrounding tissues.
3. Nematic liquid crystal are useful research tools in the application of magnetic resonance. Molecules that are dissolved in nematic liquid crystal solvents give a very highly resolved NMR spectrum exhibiting intermolecular dipole-dipole fine structures. Analysis of the spectra of molecules in liquid crystal solvents yield information regarding the anisotropy of chemical shifts, direct magnetic dipole-dipole interaction, indirect spin-spin couplings, bond angles, bond lengths, molecular order and relaxation process.
4. Liquid crystals have been used in chromatographic separations 138 as solvents to direct the course of chemical reactions and to study molecular arrangements and kinetics and as anisotropic host fluid for visible, UV and IR spectroscopy of organic molecules.

5. Liquid crystals are widely used in cosmetic industry in manufacturing of liquid crystal makeup removers, lipsticks and lip glasses containing cholesteric liquid crystals.
6. Liquid crystals are using extensively in pharmaceutical industries.
7. Liquid crystal displays are common in calculators, digital watches, oscillaographic systems, television displays using L.C. screens has also been developed. Cholesteric liquid crystals have also been used for novelty items such as toys and decorative materials.
8. Liquid crystal polymers also gained much interest on industrial applications. Polyester liquid crystals were developed for fire resistant, and are used as coating for multifibre, optical cables due to good surface roughness, low coefficient of friction. Polyesters are used for moulding with improved elastic modulus. Ferroelectric liquid crystals, mesomorphic free radicals are used for EPR study and colourless large pitch cholesteries has been developed.

Q.4. What are gels? Give their classification, properties and application.

Ans.

Gels

Gels are defined as a substantially dilute cross linked system, which exhibits no flow in steady state. Gels are mostly liquid, yet they behave like solids due to a three-dimensional cross-linked network within the liquid. It is the cross links within the fluid that gives structure to a gel (hardness) and contribute to stickiness (adhesiveness). In other words, a gel is formed when particles aggregate to such an extent forming a continuous network throughout the liquid.

A gel has an elastic behavior similar to a solid and is deformed when stress is applied to it but recovers to its original shape after removal of the stress as deformation has left the bonds between the particles intact. A gel also has viscous properties because part of the deformation is not recovered after the stress is removed and the gel flows since the bonds are broken and new bonds are formed as in a liquid when stress is applied.

If the stress is applied for a very short duration the elastic deformation will be predominant i.e. recoverable. If the stress lasts long the viscous deformation is most conspicuous *i.e.,* flow.

A gel thus shows the visco-elastic behavior which is characterized but the two rheological parameters.

Gels exhibit an elastic or storage module (G') and the viscous or loss module (G"). If the G' is greater than the G" the elastic properties prevail, and if the G' is less than the G" the viscous properties prevail. The overall resistance to deformation is expressed in the combined modulus G*. The moduli give the ratio of the stress to the relative deformation and thus have the dimension of stress e.g N.M^{-2} or Pa. They often strongly depend on the timescale of deformation.

The above reasoning holds when the deformation is about proportional to the stress (so called linear behaviour). Gels unlike solids often can be deformed considerably (e.g.by 10%) and still show linear behaviour. At larger deformation this relationship breaks down and as the bonds in the network are broken that do not reform within the time scale of the experiment. A still larger deformation soon causes yielding or breaking of the gel and the network is locally destroyed. The stress needed to do this may be called 'yield stress'. It is not a well-defined quantity as it depends much on conditions like geometry of the measuring instrument and time scale. The rheological properties will be altered when the deformation of the gel results in permanently breaking of the bonds.

The colloidal system constituting the liquid as the dispersed phase and the solid as the dispersion medium is known as gel. There are some sols that have a high concentration of dispersed solid and change spontaneously into semi solid form on cooling. These are known as gels. The process of gel formation is called **gelation**.

For example : gelatin dissolved in warm water forming a colloidal solution which when cooled sets to a jelly. Other example includes gum Arabic, agar, silicic acid, ferric hydroxide, cheese etc.

Gels are formed by the interlocking of the particles of solid dispersion medium in the form of a loose frame work inside which liquid is contained.

When the gel is allowed to stand for a long time it shrinks and loses the entire liquid held by it. This shrinking of gel is termed as syneresis or weeping.

Classification of gels : Gels may be classified into two types :

1. Elastic gels
2. Non-elastic gels

Elastic gels

(i) **Elastic Gels :** These are the gels which possess the property of elasticity. They readily change their shape on applying force and return to original shape when the applied force is removed. They change to solid mass on dehydration which can again be converted into gel by addition of water followed by heating and cooling. When these gels are placed in contact with water, they absorb water and swell. This property is called **Imbibition**.

Examples are gelatin, agar, starch etc.

(ii) **Non-elastic Gels :** These are the gels which are rigid and do not have the property of elasticity. They change into solid mass on dehydration which becomes rigid and cannot be converted into original form by heating with water.

They do not show the phenomenon of imbibition.

For example: silica gel.

Food Gels : A food gel consists of a continuous phase of inter connected particles and/or macro molecules intermingled with a continuous liquid phase such as water. Gels possess various degrees of rigidity, elasticity and brittleness depending on the type and concentration of the gelling agent, salt content and pH of the aqueous phase and temperature. Gelling agents present at levels of 10% of less may be polysaccharides, proteins or colloidal complex particles such as casein micelles. Firm gels can be prepared by few types of gums, pectins, and gelatin at levels of 1% or lower. Gels prepared with colloidal particles are generally not very rigid even when the solids content is considerably higher than 1%. Some of the gels can be melted (liquefied) and reset with the addition or removal of thermal energy and these have been designated as thermo reversible. Gels with covalent bonds between the molecules or complex particles however are generally thermo irreversible.

Conditions for the transformations of a sol into a gel are :

- Temperature change
- Chemical alteration of gelling agent

- Reduction in number of charged groups by adjustment of pH or addition of salt and addition of a water competitive compound such as sugar.

During the sol gel transformation, a three-dimensional network is formed involving interaction of groups of polymer chains or particles to form cross linkages at the site of junction zones. The aqueous phase is entrapped in the interstitial areas of the structure. In some gelling agents, the junction zones consist of micro crystallites involving specific chain units arranged in a crystal-like fashion. Bonds in the junction zones are electrostatic, hydrophobic, covalent and hydrogen bonds. Thermo reversible gels have preponderance of intermolecular hydrogen bonds whereas in a protein gel a few disulfide linkages per polymer chain may be sufficient to render them thermo irreversible.

Properties of Gels

1. **Hydration :** A completely dehydrated elastic gel can be regenerated by addition of water. But once a nonelastic gel is freed from moisture, addition of water will not bring about gelation.
2. **Swelling :** Partially dehydrate elastic gels imbibe water when immersed in the solvent. This causes increase in the volume of the gel and process is called Swelling.
3. **Syneresis :** Many inorganic gels on standing undergo shrinkage which is accompanied by exudation of solvent. This process is termed Syneresis.
4. **Thixotropy :** Some gels are semisolid when at rest but revert to liquid sol on agitation. This reversible sol-gel transformation is referred to as Thixotropy. Iron oxide and silver oxide gels exhibit this property. The modern thixotropic paints are also an example.

Applications of gels : The process of gel formation is used in the following ways :

1. Gelatin and agar-agar gels are employed in laboratories of making liquid junctions.
2. Silica gel is used in laboratory as a dehydrating agent in desiccator.
3. Silica gel is employed in industry and also used to support the platinum catalyst. It also acts as a resistance to catalytic poisoning during the manufacture of H_2SO_4 form contact process.
4. Solidified alcohol, a gel, is used as fuel in picnic stoves and is made from alcohol and calcium acetate,
5. Boot-polishes and animal tissues have the gel structures.

●

UNIT-VI

Co-ordination Chemistry

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Sort out the complex salts and double salts among the following : Pot. dicyanoargentate (I), Mohr's salt, Potash alum, Pot. ferrocyanide.

Ans. *Complex salts :* Pot. dicyanoagentate (I), Pot. ferrocyanide
Double salts : Mohr's salt, Potash alum

Q.2. Does a solution of $K_4[Fe(CN)_6]$ contain Fe^{2+} ions?

Ans. No

Q.3. Name the ions present in the aqueous solution of $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Ans. K^+, Al^{3+}, SO_4^{2-}

Q.4. Sort out the cationic, anionic and neutral complexes among the following : $K_2[HgI_4], [Co(NH_3)_6]Cl_3, K_3[Fe(CN)_6], [Ni(CO)_4], [Pt(NH_3)_2Cl_2], [Fe(H_2O)_6]Cl_3$.

Ans. *Cationic :* $[Co(NH_3)_6]Cl_3, [Fe(H_2O)_6]Cl_3$;
Anionic : $K_2[HgI_4], K_3[Fe(CN)_6]$;
Neutral : $[Ni(CO)_4], [Pt(NH_3)_2Cl_2]$

Q.5. Name the ligand/ligands present in $[Pt(NH_3)_2Cl_2]Br_2$.

Ans. Ammine (NH_3), Chloro (Cl)

Q.6. What is the oxidation number of Co in $[Co(NH_3)_5NO_2]Cl_2$?

Ans. +3

Q.7. What is the number of coordination sites in :
(a) oxalato (b) ammine
(c) ethylenediamine (d) EDTA?

Ans. (a) 2 (b) 1 (c) 2 (d) 6

Q.8. What is the number of ionisable chlorine atoms in the complex $CoCl_3 \cdot 4NH_3$?

Ans. One

Q.9. How many ions would be furnished by the complex $CoCl_3 \cdot 4NH_3$?

Ans. Four

Q.10. Calculate the charge number of the complex ion furnished by the complex $K_2[HgI_4]$.

Ans. −2.

Q.11. Write the IUPAC names of the following complexes :

(a) $[Fe(H_2O)_6]Cl_3$ (b) $[CoCl_2(en)_2]$

Ans. (a) hexaaquairon (III) chloride, (b) bis(ethylenediamine) cobalt (II) chloride

Q.12. Write the IUPAC name of the complex $[CoCl(NO_2)(NH_3)_4]ClO_4$.

Ans. tetraamminechloronitrocobalt (III) perchlorate

Q.13. Write the structures of the following complexes :

(a) ammonium diamminetetra (thiocyanato-N) chromate (III)

(b) dichlorobis (ethylenediamine) cobalt (IV) sulphate

Ans. (a) $NH_4[Cr(NCS)_4(NH_3)_2]$, (b) $[COCl_2(en)_2]SO_4$

Q.14. What type of isomerism is exhibited by the following pairs of isomers?

(i) $[Pt(OH)_2(NH_3)_4]SO_4$ and $[Pt(SO_4)(NH_3)_4](OH)_2$

(ii) $[Cr(SCN)(H_2O)_5]^{2+}$ and $[Cr(NCS)(H_2O)_5]^{2+}$

(iii) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

Ans. (i) Ionisation isomerism, (ii) Linkage isomerism, (iii) Coordination isomerism

Q.15. Do square planar complexes exhibit optical isomerism?

Ans. Not commonly

Q.16. Why is the *trans*-isomer of $[Co(en)_2Cl_2]^+$ not optically active?

Ans. It possesses a plane of symmetry and is achiral.

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What are co-ordination compounds?

Ans.

Coordination Compunds

Coordination compounds are those molecular or addition compounds in which a central metal atom or ion is permanently attached to certain atoms or groups of atoms called ligands. The ligands are capable of donating atleast a pair of electrons to the central metal atom or ion and get attached to it by coordinate bonds.

Coordination compounds retain their identity even in solution and their properties are different from those of their constituent atoms or groups. For example, potassium ferrocyanide, $K_4[Fe(CN)_6]$ is a coordination compound. It ionises in solution as

$$\underset{\text{Pot. ferrocyanide}}{K_4[Fe(CN)_6]} \rightleftharpoons 4K^+ + \underset{\substack{\text{Ferrocyanide ion}\\ \text{(complex ion)}}}{[Fe(CN)_6]^{4-}}$$

Ferrocyanide ion, $[Fe(CN)_6]^{4-}$ is the complex part of this coordination compound. It consists of six cyanide ions (ligands) permanently attached to the central Fe^{2+} ion. This ion does not dissociate further in the solution and retains its identity. Moreover, the properties of $[Fe(CN)_6]^{4-}$ ion are quite different from those of Fe^{2+} and CN^- ions.

The chemistry of coordination compounds started with the brilliant work of **Alfred Werner** in 1892. This is why Werner is regarded as the **Father of coordination chemistry** and coordination compounds are usually referred to as **Werner complexes.**

Q.2. Write short notes on :

(i) Double salts.
(ii) Central metal ion.
(iii) Ligands.
(iv) Complex ion or co-ordination entity.
(v) Co-ordination and ionic spheres.
(vi) Co-ordination polyhedron.
(vii) Cationic, anionic and neutral complexes.

Ans.

(i) Double Salts

Double salts are those molecular or addition compounds which exist in the solid state but dissociate into their constituent ions when dissolved in water. Thus, double salts lose their identity in aqueous solutions. Following examples illustrate the nature of double salts.

(i) **Mohr's salt,** $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ is double salt and may be obtained by mixing the saturated solutions of ferrous sulphate and ammonium sulphate and cooling the resultant mixture.

$$FeSO_4 + (NH_4)SO_4 + 6H_2O \longrightarrow \underset{\text{Mohr's salt}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

When dissolved in water, Mohr's salt loses its identity and dissociates into its constituent ions as follows.

$$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \longrightarrow Fe^{2+} + 2NH_4^+ + 2SO_4^{2-} + 6H_2O$$

The aqueous solution of this salt gives the test of Fe^{2+}, NH_4^+ and SO_4^{2-} ions. Thus, Mohr's salt is a double salt.

(ii) **Potash alum,** $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ is another example of a double salt. It may be obtained by mixing the saturated solutions of potassium sulphate and aluminium sulphate and evaporating the resultant solution.

$$Ni(CN)_2 + 2KCN \longrightarrow \underset{\text{Potassium tetracyanonikelate (II)}}{K_2[Ni(CN)_4]}$$

When potash alum is dissolved in water, it loses its identity and dissociates into its constituent ions as shown below.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \longrightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$$

Thus, the solution of potash alum responds to the test of K^+, Al^{3+} and SO_4^{2-} ions.

Some other examples of double salts are carnallite ($KCl.\ MgCl_2 \cdot 6H_2O$), ferric alum [$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$], etc.

(ii) Central Metal Atom or Ion

The metal atom or ion to which certain atoms or groups of atoms (called ligands) are permanently attached in a coordination compound is called **central metal atom or ion.** For example, in the complex $K[Ag(CN)_2]$, Ag^+ is the central metal ion.

Any metal atom or ion which can accept electrons given by ligands can act as a central metal atom or ion and can involve in complex formation. Complexes are usually formed by transition metal atoms or ions because they possess sufficient vacant *d*-orbitals to accommodate electrons given by ligands.

(iii) Ligands

The molecular or ionic species which gets directly attached to the central metal atom or ion during the formation of a complex is called a **ligand**. For example, in the complex $K_4[Fe(CN)_6]$, CN^- ions are ligands because they get directly attached to the central Fe^{2+} ion during the formation of this complex.

Ligands attach to central metal atom or ion through coordinate bonds. Therefore, the atoms, ions or molecules which have a tendency to donate a pair of electrons to the central metal atom can work as ligands. Ligands may be both neutral as well as negatively charged. Some important ligands are :

$$\ddot{N}H_3,\ H_2\ddot{O}:,\ -\ddot{N}H_2,\ H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$$

(ethylene diamine, *en*), $:\ddot{\underset{\cdot\cdot}{F}}^-:$, CN^-, etc.

(iv) Complex ion (Coordination entity)

The electrically charged species formed by the union of a central metal atom or ion with one or more ligands is called a **complex ion**. For example, $[Fe(CN)_6]^{4-}$ ion is a complex ion. In this complex ion, the central Fe^{2+} ion is attached to six CN^- ligands. Similarly, $[Cu(NH_3)_4]^{2+}$ is a complex ion in which Cu^{2+} ion is linked to four NH_3 ligands.

A complex ion may have positive or negative charge on it. A positively charged complex ion is called **cationic complex** ion, while the negatively charged complex ion is termed as **anionic complex ion**. For example,

Cationic complex ions : $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$, $[Co(NH_3)_6]^{3+}$, etc.

Anionic complex ions : $[Fe(CN)_6]^{4-}$, $[Cu(Cl)_4]^{2-}$, $[Ag(CN)_2]^-$, etc.

While writing the formula of a complex ion, the ligands are usually written inside the parentheses, and the entire complex ion in a square bracket. The net charge present on the complex ion is written at the right hand top corner of the square bracket.

(v) Coordination and Ionic Spheres

The part consisting of the central metal atom and ligands directly attached to it (enclosed in square brackets) is called the **coordination sphere** of the complex compound, while the part which gets ionised in solution (written outside square brackets) is called the **ionic sphere** of the complex compound. For example, the complex, $[Cu(NH_3)_4]SO_4$ ionises in solution as

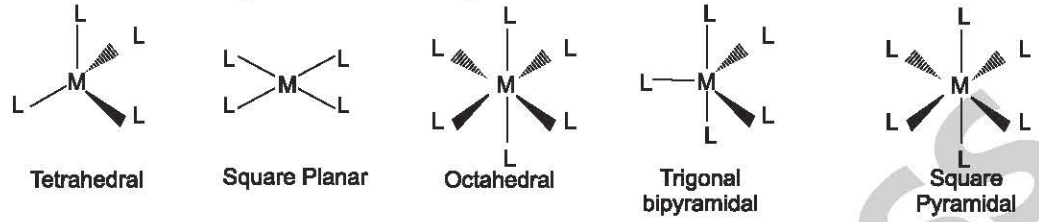
$$\underset{\text{complex compound}}{[Cu(NH_3)_4]SO_4} \rightleftharpoons \underset{\text{(coordination sphere)}}{[Cu(NH_3)_4]^{2+}} + \underset{\text{(ionic sphere)}}{SO_4^{2-}}$$

Obviously, the part $[Cu(NH_3)_4]^{2+}$ constitutes the coordination sphere while SO_4^{2-} the ionic sphere of this complex.

(vi) Coordination Polyhedron

The spatial arrangement of the ligands directly attached to the central atom or ion constitute a polyhedron about the central atom. This polyhedron is termed as **coordination polyhedron**.

The coordination polyhedron may be tetrahedral, square planar, octahedral, trigonal bipyramidal, etc., in shape as shown in Fig. 9.



Tetrahedral Square Planar Octahedral Trigonal bipyramidal Square Pyramidal

Fig. 9 : Shapes of different coordination polyhedra. M represents the central metal atom/ion and L represents a monodentate ligand

(vii) Cationic, Anionic and Neutral Complexes

Coordination compounds or complexes may be of following three types :

1. **Cationic complexes :** The complexes in which the complex ion carry a net positive charge are called cationic complexes. For example, $[Fe(H_2O)_6]Cl_3$, $[Co(NH_3)_6]Cl_3$, $[Ni(NH_3)_6]Cl_2$, etc. The complex ions present in these complexes carry a net positive charge as is clear from the following :

$$[Fe(H_2O)_6]Cl_3 \rightleftharpoons [Fe(H_2O)_6]^{3+} + 3Cl^-$$

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$

2. **Anionic complexes :** The complexes in which the complex ions carry a net negative charge are called **anionic complexes**. For example, $K_4[Fe(CN)_6]$, $K[Ag(CN)_2]$, $K_2[HgI_4]$, etc. These complexes possess anionic complex ions as is clear from the following :

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

$$K_2[HgI_4] \rightleftharpoons 2K^+ + [HgI_4]^{2-}$$

3. **Neutral complexes :** The complexes which carry no net charge are called **neutral complexes**. For example, $[Ni(CO)_4]$, $[Pt(NH_3)_2Cl_2]$, etc.

Q.3. What do you mean by co-ordination number?

Ans.

Coordination Number

The maximum numbe of ligands which can be coordinated to a central metal atom or ion is known as the **coordination number** of that central atom or ion. For example, in $K_4[Fe(CN)_6$, six CN^- ligands are coordinated to central Fe^{2+} ion. Therefore, its coordination number is six. Similarly, in $[Cu(NH_3)_4]SO_4$, the coordination number of Cu^{2+} is four. Coordination numbers of metals vary from 2 to 10 but the most common coordination numbers are 4 and 6. The coordination number of a metal ion depends mainly upon its nature, its oxidation state and on the nature of ligands surrounding it. However, coordination number may be influenced by temperature, pressure and nature of solvent. A particular metal may exhibit different coordination numbers in different complexes. For example, platinum has coordination number 4 in $[PtCl_4]^{2-}$, while coordination number 6 in complex ion $[PtCl_6]^{4-}$.

The geometry of a complex depends upon the coordination number of its central metal atom. Central metals with coordination number 6 usually form **octahedral complexes**, while those with coordination number 4 usually form **tetrahedral** or **square planar complexes.**

Q.4. Write in brief charge number of a complex ion.

Ans.

Charge Number of a Complex Ion

The net charge carried by a cmplex ion is called its **charge number**. It is equal to the algebraic sum of the charges carried by central ion and the ligands attached to it. For example, the charge number of $[Fe(CN)_6]^{4-}$ is –4. It may be calculated as shown below :

$$\text{Charge number of } [Fe(CN)_6]^{4-} = (\text{charge on } Fe^{2+}) + (6 \times \text{charge on } CN^- \text{ ion})$$

$$= (+2) + 6 \times (-1) = -4.$$

Q.5. Describe oxidation number or oxidation state of the central metal atom with examples.

Ans.

Oxidation Number of Oxidation State of the Central Metal Atom

The number which represents the electrical charge which the central atom actually has or appears to have when combined with other atoms or groups of atoms is called the **oxidation number** or the **oxidation state** of the central metal atom.

For example, the oxidation state of iron in the complex, $K_4[Fe(CN)_6]$ is +2.

The oxidation number or oxidation state of the central metal atom may be calculated according to the common rules used for the purpose which we have already studied earlier. Following examples illustrate the procedure.

1. **Oxidation number of Cu in $[Cu(NH_3)_4]SO_4$:** Suppose the oxidation number of Cu in this complex is *x*. Since it is a neutral molecule, the sum of oxidation numbers of all the species in it should be equal to zero. Hence.

   $$x + 4 \times (0) - 2 = 0 \quad \text{or} \quad x = +2$$

   Therefore, the oxidation number of Cu in this complex is +2.

2. **Oxidation number of Fe in $[Fe(CN)_6]^{3-}$ ion :** Suppose the oxidation number of iron is *x*. The sum of oxidation numbers of all the species present in it should be equal to the charge present on the ion. Hence,

   $$x + 6 \times (-1) = -3 \quad \text{or} \quad x = +3.$$

   Thus, the oxidation number of Fe in this complex ion is +3.

3. **Oxidation number of Au in $H[AuCl_4]$:** If the oxidation number of gold in this complex is *x*, we have

   $$+1 + x + 4 \times (-1) = 0 \quad \text{or} \quad x = +3.$$

   Thus, the oxidation number of Au in this complex is +3.

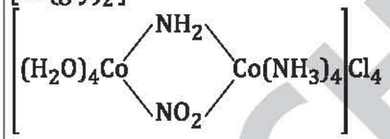
4. **Oxidation number of Ni in $[Ni(CO)_4]$:** If the oxidation number of nickel in this complex is *x*, we have

   $$x + 4 \times (0) = 0 \quad \text{or } x = 0.$$

   Thus, the oxidation number of Ni in this complex is 0.

Q.6. Write the names of the following complex compounds.

Ans.

S.No.	Complex Compound	IUPAC Name
1.	$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
2.	$Na[Ag(CN)_2]$	Sodium Dicyanoargentate (I)
3.	$Ni(CN)_4]^{2-}$	Tetracyanonickelate (II) ion
4.	$[CrF_6]^{3-}$	Hexafluorochromate (III) ion
5.	$K[PtCl_3(NH_3)]$	Potassium aminetrichloroplatinate (II)
6.	$Hg[Co(SCN)_4]$	Mercury tetrathiocyanatocobaltate (II)
7.	$[Pt(py)_4][PtCl_4]$	Tetra kis pyridineplatinum (II) tetrachloroplatinate
8.	$[Co(CO)_6]$	Hexacarbonyl cobalt (o)
9.	$[Mn_3(CO)_{12}]$	Dodecacarbonyl trimanganese (o)
10.	$[Fe(C_5H_5]_2]$	Bis (cyclopentadienyl) iron (II)
11.	$[CoCl(ONO)(en)_2]^+$	Chlorobis (ethylenediamine) nitritocobalt (III) iron
12.	$[Cr(NH_3)_4SO_4]ClO_4$	Tetraamine sulphato chromium (III) perchlorate
13.	$[Cr(PPh_3)(CO)_5]$	Pentacarbonyl triphenylphosphene chromium (II)
14.	$Fe_4[Fe(CN)_6]_3$	Ferric hexacyanoferrate (II)
15.	$Na[PtBrCl(NO_2)(NH_3)]$	Sodium amminebromochloronitroplatinate (II)
16.	$[Cu(H_2O)_2(NH_3)_4]SO_4$	Tetraaminediaqua copper (II) sulphate
17.	$[Cu(gly)_2]$	Diglycinato copper (II)
18.		Tetraaquacobalt(III)-μ-amido-μ-nitro tetraaminecobalt (III) chloride
19.	$[PtCl_2(en)_2](NO_3)_2$	Dichlorobis (ethylenediamine) platinum (IV) nitrate
20.	$K_3[Fe(C_2O_4)_3]$	Potassium trioxalatoferrate (III)

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. Describe Werner's theory of co-ordination complexes.

Ans.

Werner's Coordination Theory

Alfred Werner a Swiss chemist, in 1892 prepared a large number of coordination compounds and studied their physical, chemical and isomeric behaviour by simple experimental techniques. He isolated cobalt compounds from the reaction of cobalt chloride and ammonia.

The earlier studies of cobalt complexes were precipitation reactions, conductance measurements and isomeric behaviour.

1. **Precipitation Studies :** The number of ions furnished by a complex in a solution can be determined by precipitation reactions.

   For example :

   (a) The number of Cl^- ions in a solution of various amines were determined by the treatment with silver nitrate solution. From the amount of white precipitate of AgCl formed per mole of the compound, the number of Cl^- ions can be calculated.

(b) When the compound $CoCl_3 \cdot 6NH_3$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained from 1 mol of the compound *i.e.* all the three Cl^- ions are precipitated.

(c) When the compound $CoCl_3 \cdot 5NH_3$ is treated with excess of $AgNO_3$, 2 mol of AgCl are obtained *i.e.,* only two Cl^- ions are precipitated. This means that the compound $CoCl_3 \cdot 5NH_3$ has three ionizable chloride ions whereas in the compound $CoCl_3 \cdot 5NH_3$ only two chlorine atoms are ionizable as Cl^- ions.

$$CoCl_3 \cdot 6NH_3 \longrightarrow 3AgCl \text{ (corresponding to 3 } Cl^- \text{ ions)}$$

$$CoCl_3 \cdot 5NH_3 \longrightarrow 2AgCl \text{ (corresponding to 2 } Cl^- \text{ ions)}$$

Similarly, the number of chloride ions precipitated in the case of the compounds $CoCl_3 \cdot 4NH_3$ and $CoCl_3 \cdot 3NH_3$ have been found to be 1 and none.

2. **Conductance measurements :** The measurement of molar conductances (^m) of solutions of coordination compounds helps to estimate the number of ions furnished by the compound in solution.

   By comparing the molar conductance of the compounds with those of some known electrolytes, Werner was able to predict the number of ions present in the solution.

   For example : The complex $CoCl_3 \cdot 6NH_3$ behaved as 1 : 3 electrolyte, $CoCl_3 \cdot 5NH_3$ as 1 : 2 electrolyte, $CoCl_3 \cdot 4NH_3$ as 1:1 electrolyte.

3. **Isomers of compounds :** Werner attempted to assign structures of different coordination compounds by comparison of the number of known isomers and the number of theoretically possible structures.

Postulates of Werner's Coordination Theory

1. In co-ordination compounds, metal atoms exhibit two types of valencies namely, the primary valency and the secondary valency. The primary valency is ionizable whereas the secondary valency is non ionizable. The primary valency corresponds to oxidation state and the secondary valency corresponds to coordination number.
2. Every metal atom has a fixed number of secondary valencies *i.e.,* it he fixed coordination number.
3. The metal atom tends to satisfy both its primary as well as secondary valencies. Primary valencies are satisfied by negative ions whereas secondary valencies are satisfied either by negative ions or by neutral molecules. In certain cases, a negative ion may satisfy both types of valencies.
4. The secondary valencies are always directed towards the fixed position in space and this leads to definite geometry of the coordination compound. Secondary valencies have characteristic spatial arrangements corresponding to different coordination numbers. Spatial arrangements are called **coordination polyhedral.**

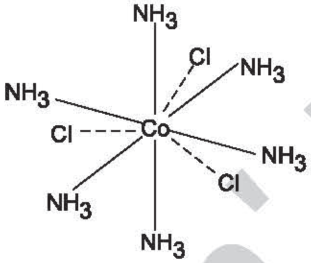
   For example : If a metal ion has six secondary valencies, these are arranged octahedrally around the central metal ion. If the metal ion has four secondary valencies, these are arranged in either tetrahedral or square planar arrangement around the central metal ion. The secondary valencies, thus, determine the stereochemistry of the complex.

Thus, a metal atom exhibits primary valencies in the formation of its salts (*e.g.,* $CoCl_3$, $AgNO_3$) while the metal atom exhibits its secondary valencies in the formation of its complex ions *e.g.,* : $[Co(NH_3)_6]^{3+}$, $[Ag(NH_3)_2]^+$

Structures of Coordination Compounds on the Basis of Werner's Theory

1. **$COCl_3 \cdot 6NH_3$:** Cobalt has primary valency (oxidation state) of three and secondary valency (coordination number) six. Secondary valencies are represented by thick lines (—) and primary valencies are shown by dotted lines (....). In the complex, all the 6 secondary valencies are occupied by six NH_3 molecules. The Cl^- ions are bonded to Co by three primary valencies. These chloride ions are ionizable and therefore can be precipitated on the addition of silver nitrate. The central metal ion and the neutral molecules or ions (ligands) satisfying secondary valencies are written in a square bracket while writing the formula of the complex compound.

   Thus, the coordination compound may be formulated as $[Co(NH_3)_6]Cl_3$.

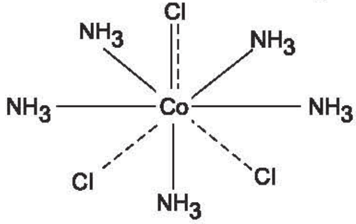
   The primary valencies are ionizable and therefore, all the chloride ions would get precipitated on the addition of silver nitrate.

   The species within the square brackets are also called **coordination entities** (or **complexes**). The ions outside the square brackets are called **counter ions.** Thus, in the coordination compound $[Co(NH_3)_6Cl]_3$, $[Co(NH_3)_6]^{3+}$ represents coordination entity and $3Cl^-$ ions represent counter ions.

   The ionization of the coordination compound is written as :

   $$[Co(NH_3)_6Cl]_3 \Rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$$

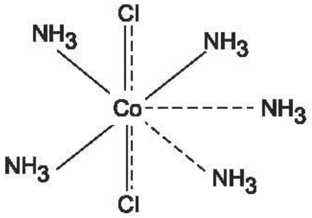
2. **$CoCl_3 \cdot 5NH_3$:** In this compound, the coordination number of cobalt is 6 but now five positions are occupied by NH_3 molecules and the sixth position by one of the chloride ions. This chloride ion has dual character as it satisfies secondary as well as a primary valency as indicated by a full line as well as a dotted line. The two Cl^- ions satisfy the remaining two primary valencies of cobalt. This satisfies 6 secondary and 3 primary valencies of cobalt. However, on ionization, only two Cl^- ions will be precipitated because one Cl^- ion which also satisfied secondary valency, will not be precipitated.

   Thus, the coordination compound may be formulated as $[CoCl(NH_3)_5]Cl_2$ which has $[CoCl(NH_3)_5]^{2+}$ complex entity and $2Cl^-$ ions as counter ions. The ionization of the coordination compound may be written as :

   $$[CoCl(NH_3)_5]Cl_2 \Rightarrow [CoCl(NH_3)_5]^{2+} + 2Cl^-$$

3. **$CoCl_3 \cdot 4NH_3$:** In the compound $CoCl_3 \cdot 4NH_3$, two chloride ions exhibit dual character of satisfying both primary and secondary valencies. It will give precipitate with silver nitrate corresponding to only one Cl^- ion and the number of ions in this case is 2.



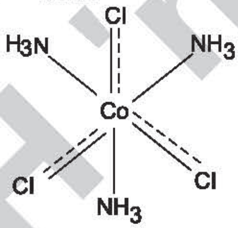
It may be formulated as

$$[CoCl_2(NH_3)_4]Cl \Rightarrow [CoCl_2(NH_3)_4]^+ + Cl^-$$

4. **$CoCl_3 \cdot NH_3$:** In the compound $CoCl_3 \cdot 3NH_3$, three chloride ions satisfy primary and secondary valencies. All the chloride ions are non-ionizable and will not be precipitated by the addition of $AgNO_3$. Therefore, the coordination compound behaves as neutral non-conducting molecule.

   It may be formulated as $[CoCl_3(NH_3)_3]$ and does not ionize.

$$[CoCl_3(NH_3)_3] \Rightarrow \text{Does not ionize}$$



$[CoCl_3(NH_3)_3]$

Behaviour of Coordination Compounds of Platinum : The important aspect of the structures of five different complexes of $PtCl_4PtCl_4$ with ammonia prepared by Werner can now be tabulated below. All these compounds, platinum, exhibit a primary valency (oxidation number) of four and secondary valency (coordination number) of six.

Formula	Present representation	Mode of ionisation	Total no. of ions (in solution)
$PtCl_4 \cdot 6NH_3$	$[Pt(NH_3)_6]Cl_4$	$[Pt(NH_3)_6]^{4+} + 4Cl^-$	5
$PtCl_4 \cdot 5NH_3$	$[PtCl(NH_3)_5]Cl_3$	$[PtCl(NH_3)_5]^{3+} + 3Cl^-$	4
$PtCl_4 \cdot 4NH_3$	$[PtCl_2(NH_3)_4]Cl_2$	$[PtCl_2(NH_3)_4]^{2+} + 2Cl^-$	3
$PtCl_4 \cdot 3NH_3$	$[PtCl_3(NH_3)_3]Cl$	$[PtCl_3(NH_3)_3]^+ + Cl^-$	2
$PtCl_4 \cdot 2NH_3$	$[PtCl_4(NH_3)_2]$	Does not ionise	0
K_2PtCl_6	$K_2[PtCl_6]$	$2K^+ + [PtCl_6]^{2-}$	3

Evidence for Werner's Theory

1. **Chloride ion activity :** Werner's theory of coordination compounds of CoCo(III) and PtPt(IV) with ammonia explains a different number of ionizable chloride ions in

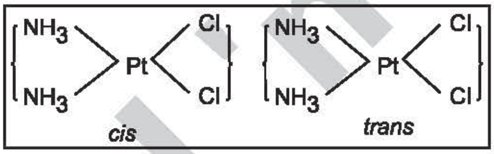
different complexes. He was also able to correctly assign whether a particular chloride ion only satisfied the primary valency or had a dual role.

2. **A total number of ions formed :** The total number of ions formed by a complex proposed by Werner is found to be following the molar conductivity of its solution.
3. **Number and type of isomers :** The number and structure of isomers proposed by Werner were found to be following the observed fact.

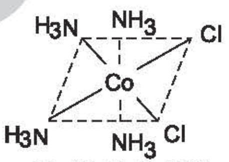
Applications of Werner's Theory : Some of the applications of Werner's theory of coordination compounds are listed below :

1. It predicts the exact structure of each complex.
2. It explains why a particular metal atom and particularly ligand form different complexes. It also explains the different properties of each complex.
3. It predicts the structure of different complexes with C.N. 44 and 66.
4. The last postulate of Werner's theory explained isomerism and predicted the existence of isomerism of types that had not previously been observed. Werner showed that the complex of divalent platinum $[Pt(NH_3)_2Cl_2][Pt(NH_3)_2Cl_2]$;existence in cis - and trans - isomeric forms.

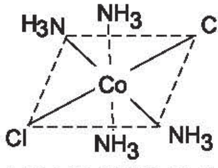
1. isomeric forms.



The existence of the isomerism established the proof of geometrical structures of these complexes, viz, the existence of the cis- and trans- isomers of the above complex indicates the planner arrangement of the coordination groups around platinum because if the arrangement were tetrahedral, then groups could be interchanged and only structure should exist. Hence isomerism would not have been possible. Similarly, Werner suggested that the two compounds (violet and green) of these compositions $CoCl_2 \cdot 4NH_3 CoCl_2 \cdot 4NH_3$ are due to cis- and trans - isomerism. The six coordination groups are at the corners of an octahedron.



cis- isomer (violet)



trans-isomer (green)

Werner's contribution is a unique one. The fundamental postulates proposed by Werner are as valid today as when they were presented over 70 years ago, despite the tremendous advances in theory, the remarkable increase in the number of coordination compounds and enormous data of such compounds.

Limitations of Werner's Theory of Coordination Compounds

1. It could not explain the inability of all elements to form coordination compounds.
2. Werner's coordination theory failed to explain the bonding nature between the central metal atom and the ligands.

3. Werner's coordination theory failed to explain the geometry of complexes when secondary valency was equal to 44.
4. It does not explain the colour, the magnetic and optical properties shown by coordination compounds.

Q.2. What do you mean by ligands? Describe various types of ligands.

Ans.

Ligands

Polar molecules or anions having at least one lone pair of electrons, are known as ligands. In ligand, an atom which gives electron lone pair to the central ion to form coordination bond is known as donor atom.

For example : In $[Ag(NH_3)_2]^+$ or $[H_3N \rightarrow Ag^+ \leftarrow NH_3]$, Ag^+ is central atom, NH_3 is ligand and N is donor atom.

Types of Ligands

On the basis of number of one or more donor atom, ligands are classified as following :

1. **Monodentate Ligands :** Ligands having only one donor atom and this donor atom is bounded to the metal ion, are known as mondentate ligands.

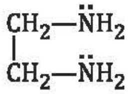
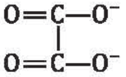
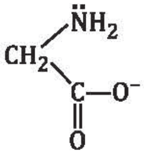
   Some common monodentate ligands are given in the table 1 :

Table 1

Monodentate Ligand	Name	Donor Atom	Charge
$H_2\ddot{O}:$	Aqua	O	0
$\ddot{N}H_3$	Amine	N	0
CO	Carbonyl	O	0
$\ddot{P}H_3$	Phosphene	P	0
$C_5H_5\ddot{N}$ or *py*	Pyridine	N	0
$(C_6H_5)_3P$ or Ph_3P	Triphenyl Phosphene	P	0
NO	Nitrosyl	N	0
X^-	Halo	X	– 1
OH^-	Hydroxo	O	– 1
$\overset{\ominus}{C}N$	Cyano	C	– 1
$\overset{\ominus}{N}C$	Isocyano	N	– 1
NO_2^-	Nitro	N	– 1
ONO^-	Nitrito	O	– 1
H^-	Hydrido	H	– 1
NH_2^-	Amido	N	– 1
O_2^{2-}	Peroxo	O	– 1
O^{-2}	Oxo	O	– 2
CO_3^{2-}	Carbonato	O	– 2
SO_4^{2-}	Sulphato	O	– 2
NH^{2-}	Amido	N	– 2
S^{2-}	Sulphido	S	– 2
N^{3-}	Azido	N	– 3
P^{-3}	Phosphedo	P	– 3

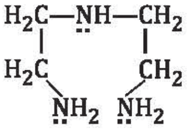
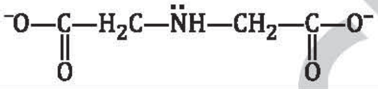
2. **Bidentate Ligand :** Ligands having two donor atoms.

Table 2

Bidentate Ligand	Name	Donor Atom	Charge
 $\mathrm{CH_2{-}\ddot{N}H_2 \mid CH_2{-}\ddot{N}H_2}$	Ethylene diamine (en)	N	0
 $\mathrm{O{=}C{-}O^- \mid O{=}C{-}O^-}$	Oxalato (*ox*)	O	– 2
	Glycinato (gly)	N and O	– 1

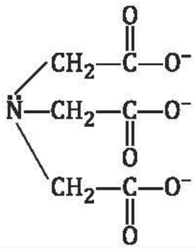
3. **Tridentate Ligand :** Ligands which have three donor atom.

Table 3

Tridentate Ligand	Name	Donor Atom	Charge
	Diethylene Triamine	N	0
 $\mathrm{^-O{-}\underset{\Vert \atop O}{C}{-}H_2C{-}\ddot{N}H{-}CH_2{-}\underset{\Vert \atop O}{C}{-}O^-}$	Ammino-diacetato	N and O	–2

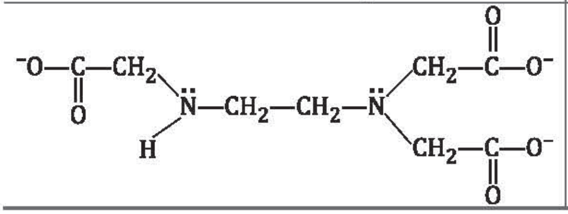
4. **Tetradentate Ligand :** Ligands which have four donor atoms.

Table 4

Tetradentate Ligand	Name	Donor Atom	Charge
$\mathrm{\ddot{N}H_2{-}CH_2{-}CH_2{-}\ddot{N}H{-}CH_2{-}CH_2{-}\ddot{N}H{-}CH_2{-}CH_2{-}\ddot{N}H_2}$	Triethylene Teramine	N	0
	Nitrilo Triacetato	N and O	– 3

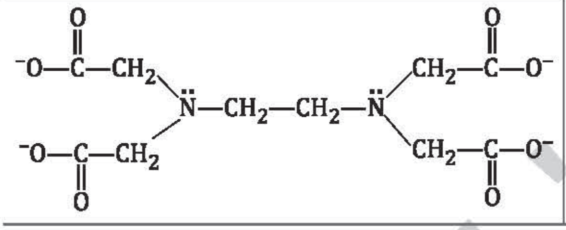
5. **Pentadentate Ligand :** Ligands which have five donor atoms

Table 5

Pentadentate Ligand	Name	Donor Atom	Charge
	Ethylene diamine tri acetato $(EDTA)^{-3}$	N and O	– 3

6. **Hexadentate Ligand :** Ligands which have six donor atoms.

Table 6

Hexadentate Ligand	Name	Donor Atom	Charge
	Ethylene diamine tetra acetato $(EDTA)^{-4}$	N and O	– 4

Q.3. Describe the IUPAC momenclature of co-ordination compounds. How to write the formula of a simple mononuclear complex from its IUPAC name? Give some examples.

Ans.

Nomenclature of Coordination Compounds

Coordination compounds are named according to the IUPAC system of nomenclature suggested in 1957 and later on modified in 1959. *The Inorganic Nomenclature Committee of the International Union of Pure and Applied Chemistry (IUPAC)*, further modified the system of nomenclature of coordination compounds in 1990. The procedure of the IUPAC nomenclature of coordination compounds according to the latest system is described below.

1. Rules of Naming the Coordination Compounds

According to the latest IUPAC recommendations, following rules are observed for naming the coordination compounds.

1. **Order of naming ions :** In ionic complexes, the positive ion (cation) is named first followed by the name of the negative ion (anion). The name is started with a small letter and the complex part is written as a single word. The names of non-ionic complexes are written as single words.

   For example, the complex $K_4[Fe(CN)_6]$ ionises as

   $$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

   Obviously, it is an anionic complex. Its positive part consists of K^+ ions, while the negative part $[Fe(CN)_6]^{4-}$ ion. Therefore, its IUPAC name consists of the name of positive part (K^+) followed by the name of negative part, *i.e.*, $[Fe(CN)_6]^{4-}$. Similarly for the complex $[Fe(H_2O)_6]Cl_3$, the name of the positive part, *i.e.*, $[Fe(H_2O)_6]^{3+}$ will be written first and it will be followed by the name of the negative part, *i.e.*, Cl^- ion.

2. **Nomenclature of ligands :** Different types of ligands are named as follows :

(a) **Neutral ligands** are named as molecules. For example,

CO	carbonyl	$NH_2CH_2CH_2NH_2$	ethane-1, 2-diamine or ethylenediamine (en)
CS	thiocarbonyl	C_5H_5N	pyridine
NO	nitroslyl	$(CH_3)_3P$	triphenylphosphine

Water (H_2O) and ammonia (NH_3), when used as ligands, are assigned special names. The ligand H_2O is named as aqua and the ligand NH_3 is named as **ammine**.

(b) **Negative ligands** are named by putting a suffix-o to the respective name of the group. For example,

Cl^-	chlorido	OH^-	hydroxo
Br^-	bromido	O^{2-}	oxo
I^-	iodido	SCN^-	thiocyanato
CN^-	cyano	$C_2O_4^{2-}$	oxalato
SO_4^{2-}	sulphato	$(O—O)^{2-}$	peroxo
CH_3COO^-	acetato	SO_3^{2-}	sulphito
S^{2-}	sulphido	NH_2^-	amido
N_3^-	azido	NO_3^-	nitrato
CO_3^{2-}	carbonato	NO_2^-	nitro
$S_2O_3^{2-}$	thiosulphato	ONO^-	nitrito

(c) **Positive ligands** occur very rarely in complexes. These are named by putting a suffix-ium to the respective name of the group. For example,

NO^+	nitrosonium	$NH_2\overset{+}{N}H_3$	hydrazinium
NO_2^+	nitronium		

3. **Mode of attachment of an ambident ligand :** Some monodentate ligands contain more than one donor atom and can attach themselves to the central metal atom through any of its donor atoms. Such ligands are called **ambident ligands**. In such a case, the name of the ligand is written in the following two ways :

(i) The name of the ligand is followed by the symbol of the atom through which it gets attached to the central metal atom. For example, the ligands SCN^- is an ambident ligand and can get attached through S as well as through N. Therefore, it is named as **thiocyanato-S** or **thiocyanato-N** depending upon its mode of linkage.

(ii) The different modes of attachment of an ambident ligand are also expressed by giving different names to the ligand for different modes of attachment. For example, the ligand NO_2^- can attach either through N (as $-NO_2^-$) or through O (as $-ONO^-$). It is designated as **nitro** and **nitrito** depending upon its mode of attachment through N and O respectively.

4. **Number of ligands :**
   (i) When two or more ligands of the same type occur in the same complex, the prefixes di, tri tetra, penta, hexa, etc., are used to indicate their number.

   For example, in the complex $[Fe(H_2O)_6]Cl_3$, there are six H_2O ligands. Therefore, the suffix **hexa** will be added to the name of the ligand, *i.e.*, aqua and the ligands present will be expressed as **hexaaqua**. Similarly, the two NH_3 ligands present in the complex, $[Ag(NH_3)_2]Cl$ will be named as **diammine**.

   (ii) When the name of a polydentate ligand includes a numerical prefix such as di, tri etc. (*e.g.*, ethylenediamine, ethylenediaminetetraacetate, etc.), the suffixes bis, tris, tetrakis, pentakis, hexakis, etc., are used to describe two, three, four, five, six, etc., ligands respectively. In such a case, the name of the ligand is written within brackets without any hyphens. For example, the complex $[Cu(en)_2]SO_4$ contains two ethylenediamine ligands. In this case, the ligands present will be described as bis **(ethylenediamine)**.

   (iii) The prefixes bis, tris, etc., are also used to indicate the number of some monodentate ligands such as methylamine because the use of prefixes di, tri, etc., in such a case may create unnecessary confusion.

5. **Order of naming ligands :** When more than one type of ligand are present in a complex, they are named in the alphabetical order regardless of the nature of charge present on them. The names of all ligands are written as a single word without any separation by hyphens. Following examples illustrate the procedure.
   (a) The ligands present in the complex $[Co(Cl)(CN)(NO_2)(NH_3)_3]$ will be named as *triamminechloridocyanonitrito*.

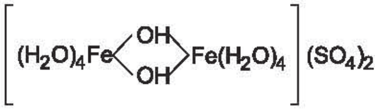
   (b) The ligands present in the complex $[Pt(NH_3)_4(NO_2)(Cl)]^{2+}$ will be named as *tetraamminechloridonitrito*.

   (c) The ligands present in the complex $[Cr(H_2O)_5(Cl)]Cl_2$ will be named as *pentaaquachlorido*.

   It is to be noted that the prefixes di, tri, etc., are not taken into account while arranging the ligands in alphabetical order.

6. **Nomenclature of bridging ligands :** A bridging ligand is indicated by adding the prefix μ before the name of the ligand. The name of the ligand is separated from μ by a hyphen. Bridging ligands are also written in the alphabetical order with the names of other ligands present in the complex. If the complex contains two or more similar bridging ligands, the prefixes di, tri etc., are used to indicate their number.

   For example, the complex contains two OH bridging and eight H_2O non-bridging ligands. This complex will be named as *tetraaquarion (III)-μ-dihydroxotetraaquairon (III) sulphate.*



7. **Nomenclature of central metal ion :** The procedure of naming the central metal ion depends upon the nature of the complex.

   (i) **Cationic and neutral complexes :** When the complex is cationic or neutral, the central metal atom or ion is described by its common name as used in other compounds. The name of the metal atom or ion is followed by its oxidation state (in the complex). The oxidation state of the metal atom or ion is written in Roman numeral and is enclosed within brackets.

   For example, in the complex $[Ag(NH_3)_2]Cl$, the central metal ion is Ag^+ and its oxidation state is +1. It will be named as **silver (I)**. Similarly, the metal ion present in the complex $[Fe(H_2O)_6]Cl_3$ will be named as **iron (III)** as its oxidation state in the complex is +3.

   (ii) **Anionic complexes :** When the complex is anionic, the name of the central metal atom or ion ends with the suffix, **ate** and is followed by its oxidation state written in Roman numeral and enclosed within brackets.

   For example, the central metal ion present in the complex $K_4[Fe(CN)_6]$ will be named **as ferrate** (II). Similarly, the central metal ion present in the complex $K[Ag(CN)_2]$ will be named as **argentate** (I).

8. **Nomenclature of complex ions :** The nomenclature of complex ions depends upon their nature.

   (a) **Cationic complex ions and neutral complex species :** Such complexes are named by writing the number and names of ligands followed by the name of the central metal atom or ion which is further followed by its oxidation state in Roman numeral enclosed in brackets. For example,

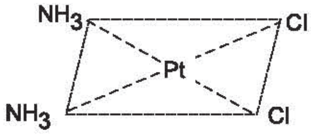
$[Cu(NH_3)_4]^{2+}$	tetraamminecopper (II) ion
$[Fe(H_2O)_6]^{3+}$	hexaaquairon (III) ion
$[CoCl_2(en)_2]$	dichloridobis (ethane-1, 2-diamine) cobalt (II)

   (b) **Anionic complex ions :** Such species are named by writing the number and names of ligands followed by the name of the central metal ion ending with ate which is further followed by its oxidation state in Roman numeral enclosed in brackets. For example

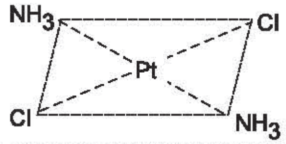
$[Fe(CN)_6]^{3-}$	hexacyanoferrate (III) ion
$[HgI_4]^{2-}$	tetraiodomercurate (II) ion
$[AuCl_4]^-$	tetrachloroaurate (III) ion

9. **Nomenclature of geometrical isomers :** A large number of complexes show geometrical isomerism and exist in *cis* and *trans* forms. The *cis* and *trans* forms of a complex are named by prefixing the name of the complex by the word cis or trans as the

case may be. The prefixes cis and trans are separated from the name of the complex by hyphens. For example,

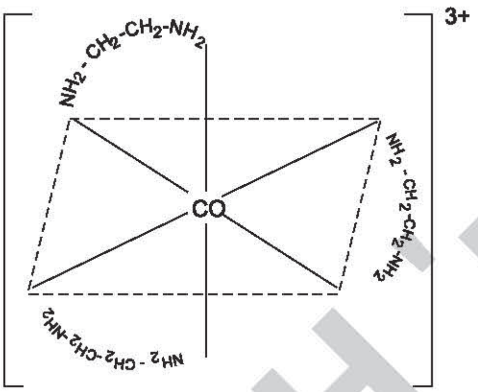


cis-diamminedichloridoplatinum (II)

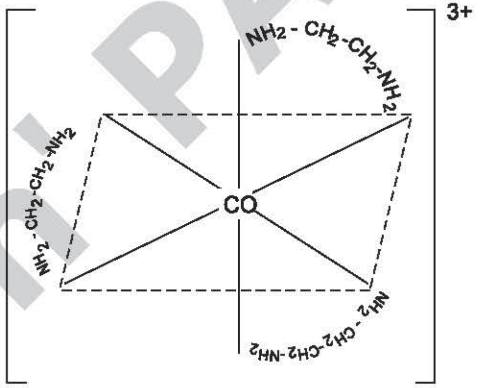


trans-diamminedichloridoplatinum (II)

10. **Nomenclature of optical isomers :** A large number of complexes also show optical isomerism and exist in enantiomeric forms. The dextro and laevo-rotatory optically active complexes are named by prefixing their names either by *d*- and *l*- or by (+) and (–) respectively. For example,



d-tris (ethane- 1,2diamine) coblalt (III) ion
or(+)-tris (ethane -1,2- diamine)cobalt(III) ion



l-tris (ethane- 1,2diamine) coblalt (III) ion
or(-)-tris (ethane -1,2- diamine)cobalt(III) ion

2. Nomenclature of Simple Mononuclear Complexes

The nomenclature of simple mononuclear (containing only one acceptor metal ion) complexes depends upon whether they are cationic or anionic.

1. **Nomenclature of cationic complexes :** The cationic complexs are named by writing the name of the complex cation (as described above) followed by the name of the anion present in the complex. Thus, following sequence is observed while writing the name of a cationic complex.

Number and name of ligands	Common name of the central metal atom or ion	(oxidation state in Roman numeral)	Name of the anion

Following examples illustrate the procedure

Cationic Complex	IUPAC Name
$[Cu(NH_3)_4]SO_4$	tetraamminecopper (II) sulphate
$[Ag(NH_3)_2]Cl$	diamminesilver (I) chloride
$[Fe(H_2O)_6]SO_4$	hexaaquairon (II) sulphate
$[Fe(H_2O)_6]Cl_3$	hexaaquairon (III) chloride
$[Co(NH_3)_6]Cl_3$	hexaamminecobalt (III) chloride

$[Cr(Cl)(H_2O)_5]Cl_2$	pentaaquachloridochromium (III) chloride
$[Co(Cl)(NO_2)(NH_3)_4]ClO_4$	tetraamminechloridonitrocobalt (III) perchlorate
$[Cr(en)_3]Cl_3$	tris(ethylenediamine)chromium (III) chloride
$[Co(Cl)_2(en)_2]SO_4$	dichlorobis (ethane-1, 2-diamine) cobalt (IV) sulphate
$[Co(Cl)(ONO)(en)_2]Cl$	chlorobis (ethane-1, 2-diamine) nitritocobalt (III) chloride

It is to be noted that the name of the anion present in a cationic complex is not prefixed by the numerical prefixes such as di, tri, etc., even when there are more than one anion present in the complex.

2. **Nomenclature of anionic complexes :** The anionic complexes are named by writing the name of the cation present in the complex followed by the name of the complex anion (as described earlier). Thus, following sequence is observed while writing the name of an anionic complex.

Name of the cation	Number and name of ligands	Name of the central metal ion with suffix are	(Oxication state in Roman numeral)

Following examples illustrate the procedure.

Anionic Complex	**IUPAC Name**
$K[Ag(CN)_2]$	potassium dicyanoargentate (I)
$H[AuCl_4]$	hydrogen tetrachloridoaurate (III)
$K_3[AgF_4]$	potassium tetrafluoridoargentate (I)
$K_4[Fe(CN)_6]$	potassium hexacyanoferrate (II)
$K_3[Fe(CN)_6]$	potassium hexacyanoferrate (III)
$K_2[HgI_4]$	potassium tetraiodidomercurate (II)
$K_3[Al(C_2O_4)_3]$	potassium trioxalatoaluminate (III)
$K_3[Co(CN)_5NO]$	potassium pentacyanonitrosylcobaltate (II)
$K[PtCl_3(NH_3)]$	potassium amminetrichloridoplatinate (II)
Dextro $K_3[Ir(C_2O_4)_3]$	potassium *d*-trioxalatoiridate (III)
$NH_4[Cr(NCS)_4(NH_3)_2]$	ammonium diamminetetra (thiocyanato-N) chromate (III)
$Na_2[Ni(EDTA)]$	sodium (ethane-1, 2-diamine) tetraacetatonickelate (III)

It is to be noted that the name of the cation present in an anionic complex is not prefixed by numerical prefixes such as di, tri, etc., even when there are more than one cation present in the complex.

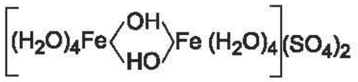
3. Nomenclature of Complexes Containing Complex Cationic and Anionic Species

The coordination compounds containing complex cations and complex anions are also quite common. Such coordination compounds are named by writing the name of the complex cation followed by the name of the complex anion. The complex cation and complex anion are named exactly in the same way as described earlier. Following examples illustrate the procedure.

$[Cr(NH_3)_6][Co(CN)_6]$	hexaamminechromium (III) hexacyanocobaltate (III)
$[PtCl_2(NH_3)_4][PtCl_4]$	tetraamminedichloridoplatinum (IV) tetrachloridoplatinate (II)
$[CoCl_2(NH_3)_4]_3[Cr(CN)_6]$	tetraamminedichloridocobalt (III) hexacyanochromate (III)
$[Pt(py)_4][PtCl_4]$	tetrapyridineplatinum (II) tetrachloridoplatinate (II)
$[Co(NH_3)_6][CdCl_5]$	hexaamminecobalt (III) pentachloridocadmate (II)

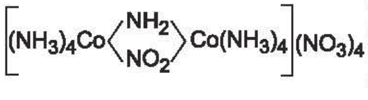
4. Nomenclature of Bridged Polynuclear Complexes

The complexes having two or more acceptor metal atoms are called polynuclear complexes. In such complexes, two or more acceptor atoms are bridged together through certain ligands called bridging ligands. As mentioned earlier, a bridging ligand is represented by prefixing the name of the ligand by symbol μ (mu) separated by hyphens. The symbol μ is repeated before the name of each different kind of bridging ligand present in the complex. Following examples illustrate the procedure of nomenclature of bridged polynuclear complexes.



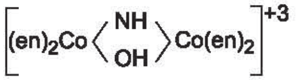
$\left[(H_2O)_4Fe\left\langle\begin{matrix}OH\\HO\end{matrix}\right\rangle Fe(H_2O)_4\right](SO_4)_2$

teraaquairon (III)-μ-dihydroxotetraquairon (III)sulphate



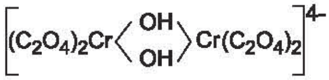
$\left[(NH_3)_4Co\left\langle\begin{matrix}NH_2\\NO_2\end{matrix}\right\rangle Co(NH_3)_4\right](NO_3)_4$

tetramminecobalte(III)-μ- amido-μ-nitrotetraamminecoblate (III) nitrate



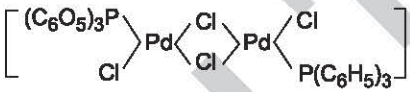
$\left[(en)_2Co\left\langle\begin{matrix}NH\\OH\end{matrix}\right\rangle Co(en)_2\right]^{+3}$

bis(ethane-1,2-diamine) cobalt (III)-μ-hydroxo μ-imido-bis (ethane-1,2-diamine) cobalt (III) ion



$\left[(C_2O_4)_2Cr\left\langle\begin{matrix}OH\\OH\end{matrix}\right\rangle Cr(C_2O_4)_2\right]^{4-}$

dioxalatochromium (III)-μ-dihydroxodioxalato chromium (III)ion



$\left[\begin{matrix}(C_6O_5)_3P\\Cl\end{matrix}\right\rangle Pd\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right\rangle Pd\left\langle\begin{matrix}Cl\\P(C_6H_5)_3\end{matrix}\right]$

choridotriphenylphosphinepallalladium (II)-μ-dichloridochlorido triphenyl phoshinepalladium (II).

5. Writing Formula of a Simple Mononuclear Complex from Its IUPAC Name

The formula of a simple mononuclear complex can easily be written if its IUPAC name is known. The rules involved and the procedure are as follows :

1. Identify the central metal and the ligands attached to it. Write their formulae in the following order :

   [Metalatom; anionic; neutral, cationic ligands]

   This constitute the coordination sphere (complex species) of the given complex. Enclose it in square brackets.

2. Calculate the charge on the complex species as follows :

   Charge on a complex species = Oxidation state of the central metal atom/ion + total charges on the ligands attached.

   It is to be noted that the oxidation state of a central metal atom/ion is always positive in a complex. Consider it while carrying out the above calculation.

3. If the charge calculated as above on the given complex species is positive, the complex under consideration is a cationic complex and would contain anions in the ionic sphere. On the other hand, if the charge is negative, it is an anionic complex and would contain cations in the ionic sphere.

4. The number of cations or anions present in the ionic sphere of the given complex can be calculated by multiplying the formula of the cation or anion (mentioned in the name)by a suitable factor in such a way that the total charge in the ionic sphere becomes equal to that of the coordination sphere.
5. In case of a cationic complex, write the ionic sphere immediately after the coordination sphere; while in case of an anionic complex, write the ionic sphere immediately before the coordination sphere. This will give the structure of the given simple mononuclear complex. Following examples illustrate the procedure.

Example 1. Give the chemical formula of potassium hexacyanoferrate (II).

Solution : As the name hexacyanoferrate (II) implies, the central metal in this complex is iron (Fe) and it is attahced to six cyanide (CN^-) ligands. The oxidation state of iron is +2.

$\therefore$ Charge on the complex species $= +2 + 6 \times (-1) = -4$

Thus, the complex species should be represented as $[Fe(CN)_6]^{4-}$. Further, the ionic sphere contains potassium (K^+) ions. In order to balance the charge, there should be four K^+ ions in the ionic sphere. Hence, the given complex will have the formula $K_4[Fe(CN)_6]$.

Example 2. Give the chemical formula of the compound nitropentaamminecobalt (III) nitrate.

Solution : The name nitropentaamminecobalt (III) implies that the given complex contains cobalt in the +3 oxidation state and it is attached to one nitro and five NH_3 ligands.

$\therefore$ Charge on the complex species $= +3 + (-1) + 5 \times (0) = +2$

Thus, the complex species should be represented as $[Co(NO_2)(NH_3)_5]^{2+}$. Further, the ionic sphere contains NO_3^- ions. In order to balance the charge, there should be two NO_3^- ions. Hence, the given complex will have the formula $[Co(NO)_2(NH_3)_5](NO_3)_2$.

Q.4. What is isomerism in co-ordination compounds? Describe structural isomerism in coordination compounds.

Ans.

Isomerism in Coordination Compounds

Two or more chemical compounds having same molecular formula but different structure or three dimensional arrangement are known as isomers and this process is known as isomerism.

These compounds show two types of isomerism :

1. Structural Isomerism.
2. Stereo Isomerism.

Structural Isomerism

Two or more chemical compounds having same molecular formula but different structures of compounds, are known as structural isomers.

Structural isomerism is categorised in following parts :

1. **Ionisation Isomerism :** Coordination compounds which have same molecular formula but give different ions in their aqueous solution are known as ionisation isomers.

   For example : Two ionisation isomers of $Co(NH_3)_5BrSO_4$ are as following :

$$[Co(NH_3)_5Br]SO_4(aq) \rightleftharpoons [CO(NH_3)_5SO_4]^+ + Br^-$$

This isomer gives pale yellow precipitate of AgBr with $AgNO_3$.

$$[Co(NH_3)_5Br]SO_4(aq) \rightleftharpoons [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$$

This isomer gives white precipitate of $BaSO_4$ with $BaCl_2$.

Some other examples are as following :

(i) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(ii) $[Co(NO_3)(NH_3)_5SO_4$ and $[Co(SO_4)(NH_3)_5]NO_3$

(iii) $[Co(en)_2Cl_2]NO_2$ and $[Co(en)_2ClNO_2]Cl$

2. **Hydrate Isomerism :** Coordination compounds which have same molecular formula but the number of water molecules is different in coordination entity and ionic entity are called hydrate isomers.

For example : Three types of hydrate isomers are found in $CrCl_3 \cdot 6H_2O$:

(i) $[Cr(H_2O)_6]Cl_3$ purple colour

(ii) $[Cr(H_2O)_5Cl_2 \cdot H_2O$ blue green colour

(iii) $[Cr(H_2O)_4Cl_2]Cl \cdot (2H_2O)$ dark green colour

3. **Linkage Isomerism :** Compounds in which monodentate ligands are ambidentate ligands *i.e.*, two donor atoms of ligand are bonded to central metal atom by coordination bonds, are known as linkage isomers.

For example :

(i) $[Cr(H_2O)_5CN]Cl_2$ and $Cr(H_2O)_5NC]Cl_2$
pentaaquacyanochromium (III) chloride — pentaaquaisocyanochromium (III) chloride

(ii) $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$
pentaaminenitrocobalt (III) chloride — pentaaminenitritocobalt (III) chloride

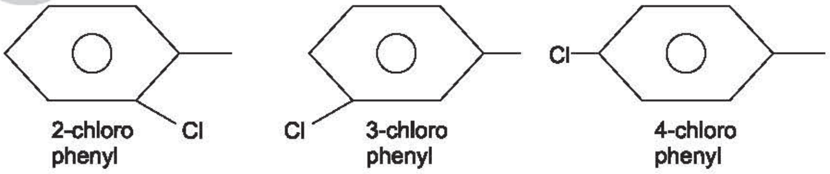
4. **Coordination Isomerism :** This type of isomerism is shown by such coordination compounds in which both cations and anions are complex ions. Complex cations and complex anions exchange the ligands.

For example :

(i) $[Co(NH_3)_6][CrCl_6]$ and $[Cr(NH_3)_6][CoCl_6]$

(ii) $[Pt(NH_3)_4][PtCl_4]$ and $[PtCl(NH_3)_3][PtCl_3NH_3]$

5. **Ligand Isomerism :** Coordination compounds is which ligands themselves show isomerism are known as ligand isomerism.



For example :

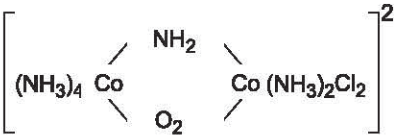
(i) $[Cr(NH_3)_5\{C_6H_4Cl(2)\}]Cl_3$

(ii) $[Cr(NH_3)_5\{C_6H_4Cl(3)\}]Cl_3$

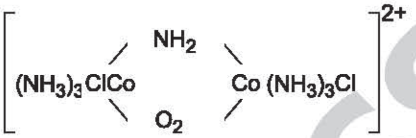
(iii) $[Cr(NH_3)_5\{C_6H_4Cl(4)\}]Cl_3$

6. **Coordination Positional Isomerism :** This isomerism is shown by coordination compounds having bridge ligand where molecular formula is same but ligand bonding in structural formulae is different.

   For example :



and



Unsymmetrical

Symmetrical

Q.5. Describe stereoisomerism (Geometrical and optical isomerism) in co-ordination compounds.

Ans.

Stereoisomerism

Coordinate bonds are directional in nature and give rise to the phenomenon of **stereoisomerism** in coordination compounds. In this type of isomerism, different atoms or groups of atoms occupy different spatial positions around the central metal atom. The isomers thus obtained are called **stereoisomers**.

Stereoisomerism is very common in coordination compounds and is studied extensively. Stereoisomerism is of two types : **geometrical isomerism** and **optical isomerism.** Both are exhibited by complex compounds. A brief account of these isomerism is given below.

I. Geometrical Isomerism

Geometrical isomerism comes into existence by the different spatial arrangement of groups around the central metal atom. Similar groups may either be arranged on the same side or on opposite sides of the central metal atom. This gives rise to two types of isomers called *cis* and *trans* isomers. When similar groups are arranged on the same side of the central metal atom, we have cis isomer and when the similar groups are spatially placed on the opposite sides, we have trans isomer.

Geometrical isomerism is common in coordination compounds and depends upon the coordination number of the central metal atom and also upon the geometry of the complex. Various cases of this types of isomerism are discussed below :

1. **Four Coordination Compounds :** Complexes with coordination number four are either tetrahedral or square planar in shape. Tetrahedral complexes can not show geometrical isomerism because all the four ligands lie at the same distance from central metal atom. Therefore, no case is observed where a tetrahedral complex is found to show this types of isomerism.

   Geometrical isomerism is very common in square planar complexes. However, all square planar complexes can not exhibit geometrical isomerism. Square planar complexes of the type Ma_4, Ma_3b and Mab_3 are unable to exist in cis and trans forms (where *a* and *b* represent monodentate ligands). Geometrical isomerism is shown only by the following types of complexes.

   (i) **Complexes of the type $(Ma_2b_2)^{n\pm}$:** Complexes of the type $(Ma_2b_2)^{n\pm}$ can exist in cis and trans forms. Cis form is obtained when both the groups *a* and both the groups *b* occupy neighbouring positions, while trans form is obtained when similar groups occupy trans positions around the central metal *M*.

For example, the cis and trans forms of complex diamminedichloridoplatinum (II), $[PtCl_2(NH_3)_2]$ are shown in Fig. 1.

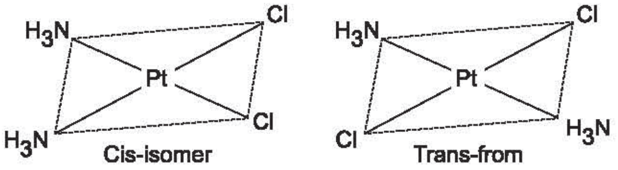


Fig. 1 : Cis and trans isomers of $[PtCl_2(NH_3)_2]$

Another complex of this type is $[Pd(NO_2)_2(NH_3)_2]$. It can also exist in cis and trans forms in the same way as shown above.

(ii) **Complexes of the type $(Ma_2bc)^{n\pm}$** : In this case, cis isomer is obtained when similar groups *a* are adjacent to each other, while the trans form is obtained when they are opposite to each other.

For example, the cis and trans forms of complex diamminebromidochloridoplatinum (II), $[PtBrCl(NH_3)_2]$ exist as shown in Fig. 2.

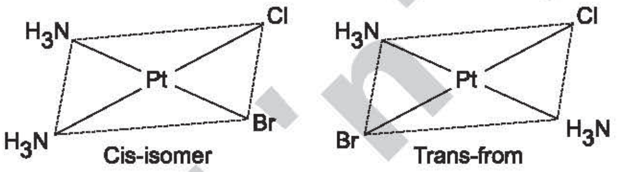


Fig. 2 : Cis and trans forms of $[PtBrCl(NH_3)_2]$

(iii) **Complexes of the type $[Mabcd]^{n\pm}$** : When all the four ligands are different, three geometrical isomers are possible in square planar complexes. An example of this type of complex is $[PtBrCl(NH_3)(py)]$. It can exist in the following three forms (Fig. 3).

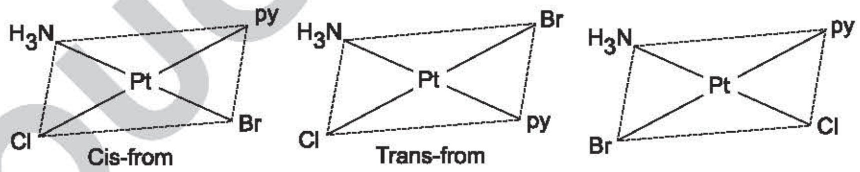


Fig. 3 : Three geometrical isomers of $[PtBrCl(NH_3)(py)]$

(iv) **Complexes of the type $[M(AB)_2]^{n\pm}$** : In the complex $[M(AB)_2]^{n\pm}$, *M* is the central metal atom, while *AB* is an unsymmetrical bidentate ligand. An example of this type of complex is $[Pt(gly)_2]$, where gly stands for glycino, $(NH_2CH_2COO^-)$ ligand. The cis and trans forms of this complex are shown in Fig. 4.

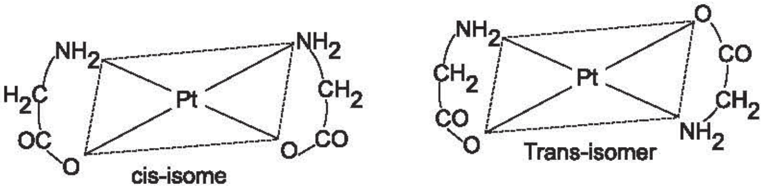


Fig. 4 : Cis and trans forms of $[Pt(gly)_2]$

2. **Six Coordination Compounds :** Complexes with coordination number six are octahedral in shape. A regular octahedron contains eight faces and six equivalent vertices. In an octahedral complex the metal is placed at the centre and six ligands occupy their positions at the vertices. Octahedral complexes of the type Ma_6, Ma_5b and Mab_5 do not show geometrical isomerism because in these complexes different spatial arrangements of ligands are not possible. Geometrical isomerism in all other types of octahedral complexes is very common. Some of the important types of octahedral complexes showing geometrical isomerism are as follows :

   (i) **Complexes of the type $[Ma_4b_2]^{n\pm}$** : In these complexes four monodentate ligands *a* and two monodentate ligands *b* are octahedrally attached to the central metal atom *M*. Cis-isomer is obtained when ligands *b* occupy adjacent (1, 2) positions, while trans-isomer is obtained when ligands *b* are opposite to each other, *i.e.*, they occupy 1, 6 positions.

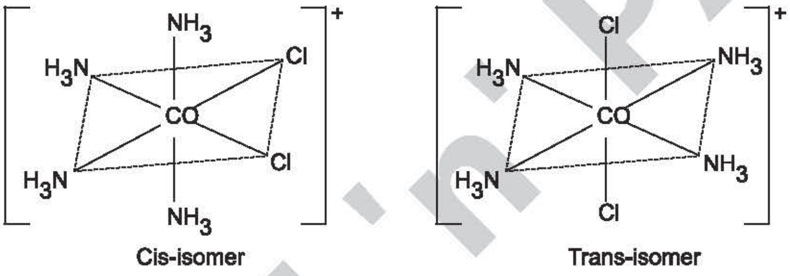


Fig. 5 : Cis and trans isomers of $[CoCl_2(NH_3)_4]^+$

An example of this type of complex is $[CoCl_2(NH_3)_4]^+$. This cis and trans forms of this complex cation are shown in Fig. 5. In this cis-isomer, the two Cl^- are in two adjacent positions (any) and hence it is designated as cis isomer. In trans isomer, the two Cl^- are in opposite positions (any) and therefore it is designated as trans isomer.

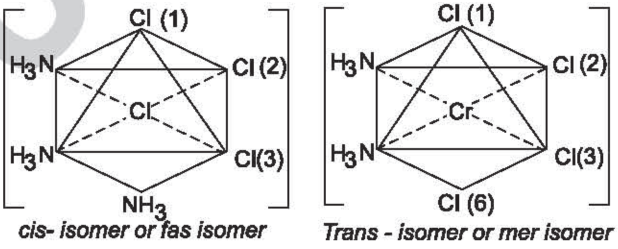


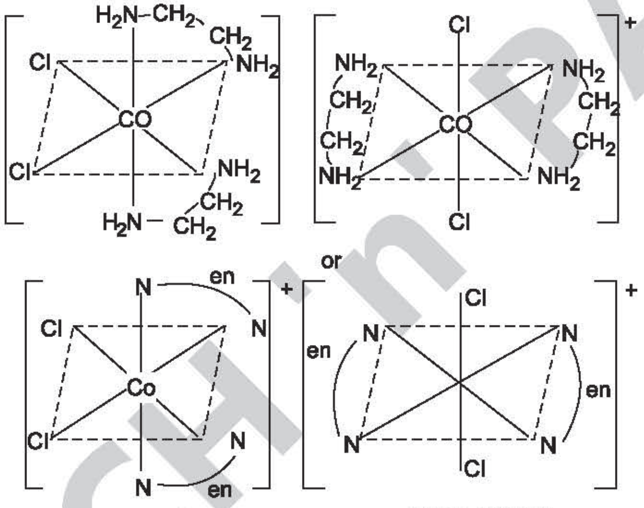
Fig. 6 : Cis and trans isomers of $[CrCl_3(NH_3)_3]$

   (ii) **Complexes of the type $[Ma_3b_3]^{n\pm}$** : An important example of this type of complexes is $[CrCl_3(NH_3)_3]$. Its cis and trans forms are shown in Fig. 6.

   In the cis-isomer, the three Cl^- are on one triangular face and the three NH_3 molecules are placed on the opposite triangular face. This isomer is designated as **facial (fac) isomer**. In trans-isomer, Cl^- are placed on the edges of the octahedron, while NH_3 molecules are present on the opposite edges. This isomer is termed as **meridonal (mer) isomer or peripheral isomer**. Other examples of this type of complexes are $[CoCl_3(NH_3)_3]$ and $[Rh(py)_3Cl_3]$.

(iii) **Complexes of the type $[M(AA)_2a_2]^{n\pm}$:** In this type of complexes, central metal atom M is attached to symmetrical bidentate chelating ligands AA and two monodentate ligands a. The two letters A and A in AA indicate the two similar coordinating atoms. These complexes exist in cis and trans forms and exhibit the phenomenon of geometrical isomerism.

An example of this type of complexes is $[CoCl_2(en)_2]^+$. The cis and trans forms of this complex are shown in Fig. 7.



Cis-isomer

Trens-isomer

Fig. 7 : Cis and trans isomers of $[CoCl_2(en)_2]^+$

Other complexes of this type are $[Co(en)_2(NO_3)_2]^+$, $[Ir(C_2O_4)_2Cl_2]^{2-}$ and $[Ir(C_2O_4)_2Cl_2]^{3-}$. These exist in cis and trans forms in the same way as shown above.

II. Optical Isomerism

Optical isomerism is shown by those compounds which possess chirality, *i.e.*, which do not possess any element of symmetry. Presence of an element of symmetry makes a molecule symmetric and renders it optically inactive. When a molecule does not possess any element of symmetry, its mirror image is not superimposable on the molecule itself. This makes the molecule optically active. Such an asymmetric molecule can exhibt the phenomenon of optical isomerism. The two forms of the molecule which are mirror images of each other are called **enantiomers.** One form rotates the plane of plane polarised light in clockwise direction, while the other in anticlockwise direction. The former is called the *d*-form, while the latter is termed as the *l*-form.

The phenomenon of optical isomerism is quite common in coordination compounds. The complexes whose molecules are asymmetric exhibit optical isomerism. The optical isomerism of various types of complexes is discussed ahead.

1. Four Coordination Compounds

1. **Square planar complexes :** In square planar complexes all the four ligands and central metal atom lie in the same plane. Therefore, they possess a plane or axis of symmetry and are generally not chiral in nature. This is why optical isomerism is not common in square planar complexes and is very rarely observed.
2. **Tetrahedral complexes :** Organic compounds having asymmetric tetrahedral carbon atoms are generally optically active. Therefore, it is expected that a tetrahedral complex with four different ligands attached to a central metal atom or ion, *i.e.*, a complex of the type $[Mabcd]^{n\pm}$ should exhibit optical activity. However, it has not been possible to resolve optically active *d*- and *l*-forms of such a complex due to its **labile nature.**

Thus, optical isomerism is not very common in both square planar as well as tetrahedral complexes. Only a very few four coordination complexes are known which exhibit optical isomerism.

2. Six Coordination Compounds

Optical isomerism is more common in six coordination complexes, *i.e.*, in octahedral complexes. Optical isomerism of some important types of octahedral complexes is discussed below :

1. **Octahedral complexes containing only monodentate ligands :** Octahedral complexes of the type $[Ma_2b_2c_2]$, $[Ma_2b_2cd]$, $[Ma_2bcde]$ and $[Mabcdef]$ do not possess any element of symmetry and should be optically active. However, none of these complexes could be resolved till now. Theoretically, octahedral complexes containing only monodentate ligands are optically active and should exist in *d*- and *l*-forms, but the paucity of adequate experimental techniques to resolve them makes their optical isomerism of little value.
2. **Octahedral complexes containing one or more symmetrical bidentate chelating ligands :** Octahedral complexes containing all the monodentate ligands could not be resolved. However, if an octahedral complex contains one or more bidentate chelating ligands, it is possible to resolve it into its optically active forms. Some examples of such complexes are given below :

   (i) **Complexes of the type $[M(AA)]_3]^{n\pm}$:** In the complexes of this type, three symmetrical bidentate chelating ligands *AA* are coordinated to the central metal atom *M*. Such complexes do not possess any element of symmetry and are optically active. Moreover, these complexes can be resolved into optical isomers.

   An example of this type of complexes is $[Cr(C_2O_4)_3]^{3-}$. It is optical active and has been resolved into *d*- and *l*-forms (Fig. 8).

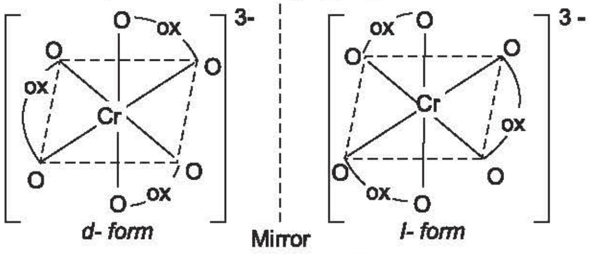


Fig. 8 : Optically active forms of complex $[Cr(C_2O_4)_3]^{3-}$ (ox-refers to bidentate oxalato ligand).

Other examples of this type are $[Co(en)_3]^{3+}$, $[Co(p_n)_3]^{3+}$, $[Pt(en)_3]^{+}$ and $[Cd(p_n)_3]^{2+}$. The optical isomers of $[Co(en)_3]^{3+}$ are shown in Fig. 9.

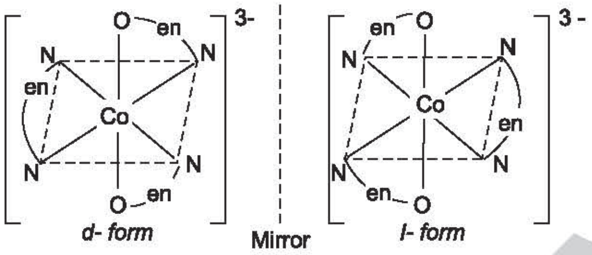
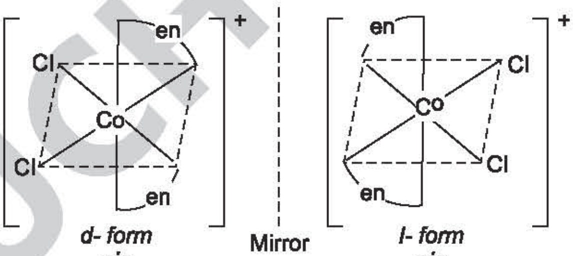


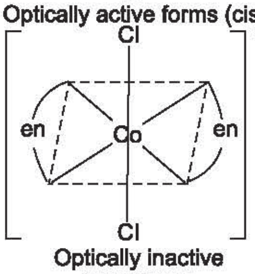
Fig. 9 : Optically active forms of $(Co(en)_3]^{3+}$

(ii) **Complexes of the type $[M(AA)_2a_2]^{n\pm}$** : The complexes in which two symmetrical bidentate chelating ligands *AA* and two monodentate ligands *a* are coordinated to central metal atom *M* also exhibit the phenomenon of optical isomerism and can be resolved into their optical isomers.

An example of this type of complexes is $[CoCl_2(en)_2]^{+}$: It exhibits both geometrical as well as optical isomerism. Its cis form is unsymmetrical, while the trans form is symmetrical because it contains a plane of symmetry. Hence, optical isomerism is shown by cis form only. The cis form has been resolved into *d*- and *l*-forms. The *d*- and *l*-forms along with the optically inactive trans form are shown in Fig. 10.



Optically active forms (cis)



Optically inactive trans forms

Fig. 10 : Optically active (cis) and optically inactive (trans) forms of the complex $[CoCl_2(en)_2)]^{+}$

(iii) **Complexes of the type $[M(AA)_2ab]^{n\pm}$** : In this case *AA* are symmetrical bidendate chelating ligands, while *a* and *b* are monodentate ligands. Such complexes exist in three forms, two are optically active (*d*- and *l*-forms) and the third one is inactive meso form. An example of this type of complexes is $[CoCl(en)_2(NH_3)]^{2+}$. Its three forms are shown in Fig. 11.

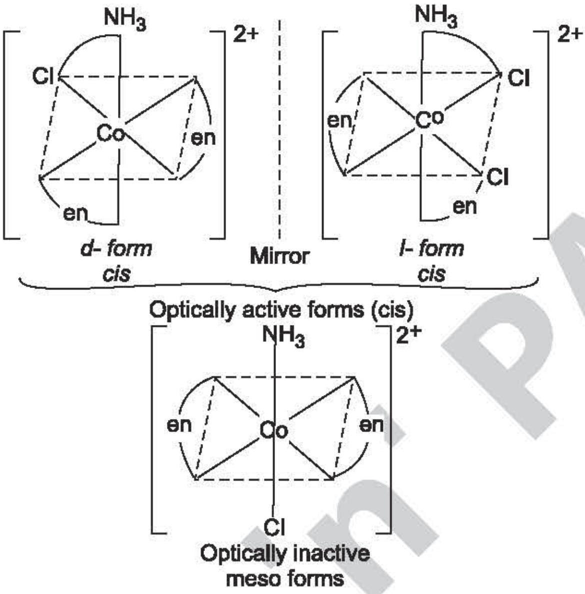


Fig. 11 : Optically active and meso forms of complex $[CoCl(en)_2(NH_3)]^{2+}$

UNIT-VII

Theories of Co-ordination Chemistry

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Name the hybridisation state of the central metal ion in the following complexes :

(i) $[Co(NH_3)_6]Cl_3$ (ii) $[Pt(NH_3)_2Cl_2]$

Ans. (i) d^2sp^3, (ii) dsp^2

Q.2. State whether a complex formed by sp^3d^2 hybridisation is a low spin or a high spin complex.

Ans. High spin complex

Q.3. The complex $[Cr(NH_3)_6]^{3+}$ involves d^2sp^3 hybridisation of the central metal ion. State whether it is an inner orbital or an outer orbital complex.

Ans. Inner orbital complex

Q.4. Among NH_3 and CN^-, which is a stronger ligand?

Ans. CN^-

Q.5. The ionic radii of Cu^{2+}, Ni^{2+} and Fe^{2+} ions are 69, 78 and 83 pm respectively. Arrange these ions in the decreasing order of the stability of the complexes formed by them.

Ans. $Cu^{2+} > Ni^{2+} > Fe^{2+}$

Q.6. Name the reagent generally used to estimate the hardness of water.

Ans. EDTA

Q.7. Name a complex used in the treatment of cancer.

Ans. Cisplatin

Q.8. Name the metals present in haemoglobin, chlorophyll and vitamin B_{12}.

Ans. Fe, Mg, Co

Q.9. Complete the following statements for the coordination entity (complex ion) $[CrCl_2(ox)_2]^{3-}$.

(a) ox is abbreviation for …… .

(b) The oxidation number of chromium is …… .

(c) The coordination number of chromium is ....
(d) ...... is a bidentate ligand

Ans. (a) oxalato ligand, (b) +3 $[x-2+2(-2)=-3, x=+3]$, (c) six, (d) Oxalato (ox)

Q.10. Specify the oxidation number of the metals in the following coordination entities :

(a) $[Co(CN)(H_2O)(en)_2]^{2+}$ **(b) $[PtCl_4]^{2-}$**
(c) $[CrCl_3(NH_3)_3]$ **(d) $[CoBr_2(en)_2]^{+}$**
(e) $K_3[Fe(CN)_6]$

Ans. (a) +3, (b) +2, (c) +3, (d) +3, (e) +3

Q.11. Specify which out of the following complex structures exhibit geometrical isomerism :

(a) linear **(b) square planar**
(c) tetrahedral **(d) octahedral**

Ans. Square planar and octahedral

Q.12. How many geometric isomers are possible in the following coordination entities?

(a) $[Cr(ox)_3]^{3-}$ **(b) $[CoCl_3(NH_3)_3]$**

Ans. (a) Nil, (b) Two

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. Write the limitations of valence bond theory.

Ans.

Limitations of Valence Bond Theory

1. This theory does not provide a quantitative interpretation of the stability of complexes.
2. The pairing of electrons against Hund's rule under the influence of a strong ligand is not properly defined in this theory. The theory does not provide a satisfactory explanation as to why at one time the electrons must be rearranged against the Hund's rule, while at the other time the electronic configuration is not disturbed. This creates unnecessary problems in deciding the geometry of a complex.
3. It is unable to interpret the absorption spectra of complexes.
4. It is unable to account for the detailed magnetic properties of complexes.
5. It lacks to explain the behaviour of d^8 ion ($Ni^{2+}, Pb^{2+}, Au^{3+}$ etc.) in forming the expected 4-coordination complexes. Why does the theory prefer square planar structure over tetrahedral or otherwise is not very logical.
6. Sometimes the theory requires the transfer of electron from a lower energy level to a higher energy level, which is not logical in the absence of an energy supplier.
7. This theory does not give a satisfactory explanation as to why some complexes are more labile (labile complexes are those complexes in which one ligand can easily be replaced by some other ligand) than the other complexes.
8. It does not explain the splitting of *d*-orbitals of central metal atom when ligands approach it.

Q.2. What are the limitations of CFT?

Ans.

Limitations of Crystal Field Theory

1. Crystal field theory assumes that metal ligand interaction is purely electrostatic. This assumption can not be said to be very realistic.
2. The theory takes into account only the *d*-orbitals of central metal atom or ion and their splitting is studied; the other orbitals, *e.g., s* and *p*-orbitals of central metal are not taken into account.
3. The theory is unable to explain why does a certain ligand cause a large splitting while the other a small, *e.g.,* the theory has no explanation why H_2O is a stronger ligand than OH^-.
4. This theory rules out the possibility of any π-bonding in complexes. This is a serious drawback of the theory because π-bonding is found to exist in complexes.
5. The theory does not give any weightage to the orbitals of ligands. Therefore, all properties related to ligand orbitals and their interaction with metal orbitals remain unexplained.

Q.3. Discuss in brief the superiority of CFT over VBT.

Ans.

Superiority of Crystal Field Theory over Valence Bond Theory

Inspite of all the above limitations, crystal field theory has an edge over valence bond theory. The crystal field theory is supposed to be superior to valence bond theory due to following facts.

1. Crystal field theory provides the fine details of magnetic properties of the complexes and gives a suitable explanation of the variation of magnetic moments with temperature. These fine details are not provided by VBT.
2. Crystal field theory provides a quantitative measure of the stability of a complex. With this measure, the geometry acquired by a particular complex can be predicted. VBT does not provide any such measure.
3. Crystal field theory gives an explanation for certain thermodynamic and kinetic properties of complexes. VBT does not provide such an explanation.
4. The observed *d-d* transitions in complexes and their colour can be explained only on the basis of crystal field theory. The VBT neither explains spectroscopic properties nor gives an adequate explanation for the colour of complexes.

Q.4. What is hard soft acid base concept?

Ans.

Hard Soft Acid Base (HSAB) Concept

Lewis acid and base theory (also known as e^- donor-acceptor theory) is a broad, widely applicable approach to the classification of chemical substances and the analysis of chemical reactions. According to this theory, a base is an electron pair donor, and an acid is an electron pair acceptor. Donation of an electron pair from base to acid results in the combining of the acid and base with a covalent bond. The bonded acid-base species is called an adduct, a coordination compound, or a complex compound.

Since the strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength. Thus, from the above criteria, an acid base reaction should be a rapid reaction. The HSAB concept is a shortening for "hard and soft (Lewis) acids and bases". Also known as the Pearson acid base concept, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. Soft Lewis base are those in which the donor atoms are easily polarized and have low electronegativity. While Hard Lewis base are those in which the donor atoms have low polarisabilities and high electronegativities. A hard Lewis acid, like hard base, is difficult to polarize, small size, high positive charge, having small size and a noble gas electronic configuration. While soft acid, like soft base, are readily polarized these have large size, low positive or zero charge and do not have a noble gas configuration.

Experimentally, it was observed that certain ligands having a tendency to form the stable complexes with the lighter metal ion like $Na^+, Li^+, Mg^{+2}, Sc^{+3}, Ti^{+4}$ etc. and certain other ligands having the tendency to form the stable complexes with the heavier metal ions like $Ag^+, Cu^{+2}, Hg^{+2}, Cu^{+2}$ etc.

On the basis of this preferential bonding nature of ligand (Lewis base and Lewis acid), Pearson had categorised both the acid and bases into three different categories.

Q.5. Describe in brief the classification of the Lewis's acid.

Ans.

Classification of the Lewi's Acid

1. **Hard acid :** All the Lewis acids having the following characteristic properties are known as hard acid :
   (i) Should exhibit the smaller size.
   (ii) Should have high +ve oxidation state.
   (iii) Polaris ability should be very low (on the basis of this property they are known as hard).
   (iv) Should have vacant *d*-orbital or approximate vacant *d*-orbital configuration (in the case of *d*-block elements)
2. **Soft acid :** All the Lewis acids having the following characteristic properties are known as soft acids :
   (i) Should exhibit larger size.
   (ii) Should have very low +ve oxidation state or zero oxidation state.
   (iii) Polaris ability should be very high (on the basis by this property they are known as soft).
   (iv) Should have filled *d*-orbital or approximate filed *d*-orbital configuration (in the case of *d*-black dements)

Borderline acids : All the Lewis acids which exhibit the properties intermediate in between the hard & soft acids are known as borderline acids. Some of the samples of hard acid, soft acid & borderline acids are given in following table :

Table : Examples of hard acid, soft acid and borderline acids

Hard acids	Soft acids	Borderline acids
Li^+	Cu^+	Fe^{+2}
Na^+	Ag^+	Co^{+2}
K^+	Au^+	Ni^{+2}
Mg^{+2}	Hg^+	Cu^{+2}
Ca^{+2}	Pt^{+2}	Zn^{+2}
Al^{+3}	Hg^{+2}	Pb^{+2}
Ba^{+2}	Pd^{+2}	Sn^{+2}
Ga^{+3}	Ed^{+2}	SO_2
La^{+3}	BH_3	Bi^{+3}
Cr^{+3}	I^+	Sb^{+3}
Cr^{+6}	Br^+	NO^+
Co^{+3}	Metal atoms at zero oxidation states	GaH_3
Fe^{+3}		$B(CH_3)_3$
Si^{+4}		
Ti^{+4}		
Ce^{+3}		
Sn^{+4}		
SO_3		
$BF_3, BCl_3, B(OR)_3, Al(CH_3)_3$		
I^{+7}		
I^{+5}		
CO_2		

Q.6. Describe in brief the classification of the Lewis's base.

Ans.

Classification of the Lewis Base

1. **Hard base :** All the Lewis bases having the following characteristic properties are known as hard base :
   (i) Donor atom of the base should be highly electronegative like F, O, N & O.
   (ii) Polaris ability of the donor atom should be very high low.
2. **Soft base :** All the Lewis bases which have the following characteristic properties are known as soft bases :
   (i) Donor atom of the base should be less electronegative.
   (ii) Polaris ability of the donor atom should be very high.
3. **Borderline base :** All the Lewis bases which have the properties intermediate the soft & hard bases are known as borderline bases.

Some of the examples of hard bases, soft bases and borderline bases can be given as :

Hard base : $H_2O, OH^-, CH_3COO^-, PO_4^{-3}, SO_4^{-2}, CO_3^{-2}, ClO_4^-, NO_3^-$, ROH, $R—O^-$ R_2O (Donor O), NH_3, $R—NH_2$, N_2H_4 (doner N), F^-, Cl^-.

Soft base : $R_2S, R—SH, R—S^-, I^-, SON^-, S_2O_3, R_3P, (RO)_3P, CN^-, RNC, CO, C_2H_4,$
C_6H_6, H^-, R^-, S^{-2}

Borderline base : $C_6H_5—NH_2, C_5H_5N, Br^-, SO_3^{-2}, NO_2^-$

Q.7. What are the theoritical basis of hardness and softness?

Ans.

Theoretical Basis of Hardness and Softness

There are some theories that can explain the interactions in between the hard acids and hard bases and vice versa. No single theory can explain this kind of interaction.

Electronegativity concept for the HSAB theory : According to the electronegativity theory, the interaction between HA and HB is ionic or electrostatic in nature. As hard acid and hard bases are small in size (HB is highly electronegative and HA is highly electropositive), the internuclear distance between them will be smaller. As a result, interaction between HA and HB will be highly stable.

Covalent concept for the HSAB theory (σ-bonding) : Soft acids have high polarising power and soft bases like I has high polarisability. Therefore, the interaction between SA and SB is covalent in nature.

Covalent concept for the HSAB theory (π-bonding) : Soft acids have fully filled d orbitals (low oxidation state) and soft bases are pi bonding ligands. Thus, SA has a good tendency to form π bonds with SB.

SECTION-C LONG ANSWER TYPE QUESTIONS

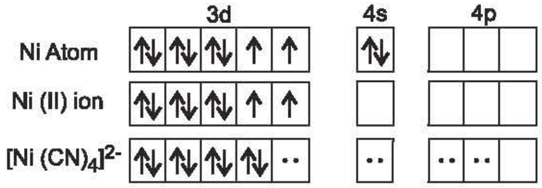
Q.1. What is valence bond theory? Describe the structure and shape of some coordination, compounds on the basis of valence bond theory.

Ans.

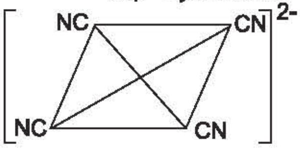
Valence Bond Theory

This theory was given by Pauling. Main points of this theory are as following :

1. Central metal atom has definite number of vacant *s*, *p* and *d* atomic orbitals as per requirement which are equal to the number of ligands.
2. *s*, *p* and *d* atomic orbitals of central ion having approximately same energy mix together to form hybridised orbitals.
3. These hybridised orbitals overlap with those orbitals of ligands which provide electron pair for bonding. The bonds so formed are directional.
4. In hybridisation, when central metal atom uses *d* orbital $\{(n-1)d\}$ of inner shell, low spin complexes are formed and when *d*-orbital (nd of outer shell) is used, high spin complexes are formed.
5. Square planar complex is obtained from dsp^2 hybridisation, tetrahedral complex from sp^3 hybridisation and octahedral complex is obtained from d^2sp^3 or sp^3d^2 hybridisation. Some examples of this theory are as following :
   (i) **$[Ni(CN)_4]^{2-}$ Tetracyanonickelate (II) :** In this, the oxidation state of Ni atom is +2. Due to the strong ligand field of CN, it pairs up the electrons in 3*d* orbitals of the Ni^{2+}. Hence, due to the dsp^2 hybridisation states of Ni^{2+}, the geometry of complex is square planar.

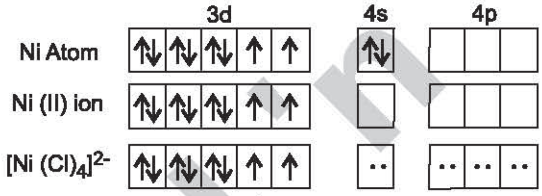


dsp^2 Hybridisation

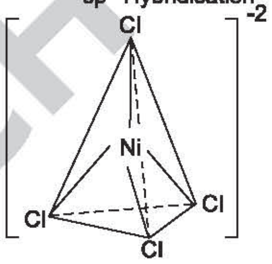


Geometry = Square planar; Bond angle = 90° ; Nature = diamagnetic.

(ii) **$[NiCl_4]^{2-}$ Tetrachloronickelate (II) :** In this, the oxidation state of Ni atom is +2. The pairing of electrons in 3*d* orbitals of Ni^{+2} does not take place due to the weak ligand field of Cl^-. Hence, due to the sp^3 hybridisation state of Ni^{+2}, the geometry of complex is tetrahedral

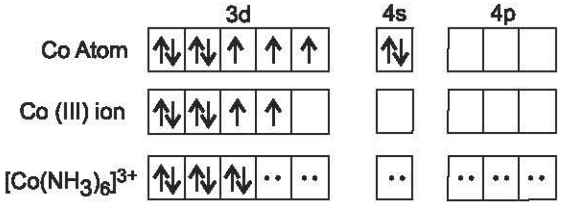


sp^3 Hybridisation

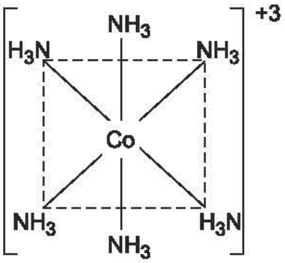


Geometry → tetrahedral; Bond angle = 109°28'; Nature - Paramagnetic

(iii) **$[Co(NH_3)_6]^{3+}$ Hexaammine cobalt (III) :** In this, the oxidation state of Co is +3. Because of the strong ligand field of NH_3, electrons pair up in the 3*d* orbitals of Co^{+3}. Hence, due to the d^2sp^3 hybridisation state of Co^{+3}, the geometry of complex is octahedral.

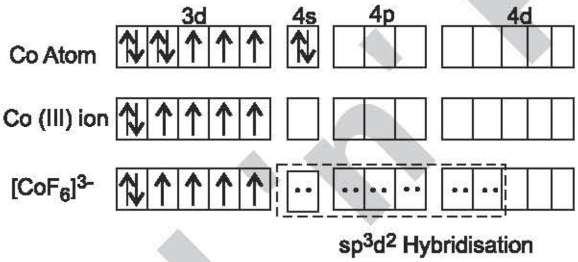


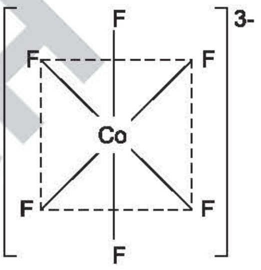
d^2-sp^2 Hybridisation



Geometry - Octahedral
Nature - Diamagnetic

(iv) **$[CoF_6]^{3-}$ Hexafluoro Cobalt (III) :** In this, the oxidation state of Co atom is +3. Because of the weak ligand field of F^-, electrons in the 3*d* orbitals of Co^{+3} do not pair up. Hence, due to the sp^3d^2 hybridisation state of Co^{+3}, the geometry of complex is octahedral.





Geometry - Octahedral
Nature - Paramagnetic

Q.2. What is crystal field theory? Give the salient features of crystal field theory.

Ans.

Crystal Field Theory

The crystal field theory was originally proposed by **Bethe** in 1929 to explain the nature of bonding in ionic crystals. Later on, the theory was applied by **Schlapp** and **Penny** (1932) and also by **Van Vleck** (1932) to account for the magnetic properties of **transition metal ions** and **their complexes.** The theory received a considerable favour from coordination chemists and it largely replaced valence bond theory in treating coordination compounds.

The crystal field theory assumes that the interaction between the metal ion and the ligands is purely electrostatic (ionic). When ligands approach central metal atom or ion, the five degenerate *d*-orbitals (*d*-orbitals having similar energies) of the central metal atom become differential, *i.e.,* they get split up into levels of different energy under the influence of the electrostatic field of ligands. This removes the degeneracy of *d*-orbitals and they get separated into two groups called t_{2g} (dxy, dyz, dzx) and e_g $(d_{x^2-y^2}, d_{z^2})$ point groups. This splitting actually depends upon the geometry of the complex. The energy separation between these two groups of splitted *d*-orbitals is usually referred to as $10Dq$ or Δ. This can be estimated from spectroscopic data and can also be calculated theoretically. Due to repulsion of ligands, the electrons of the metal ion occupy those *d*-orbitals which have their lobes farthest away from the direction of the ligand. The occupation of electrons in the *d*-orbitals is strictly according to **Hund's rule.**

Salient Features of Crystal Field Theory

The salient feaures of crystal field theory are as follows :

1. In a complex, a central metal atom or ion is surrounded by various atoms or groups of atoms called **ligands.**
2. The ligands are either negatively charged ions (like F^-, Cl^-, CN^-, etc.) or neutral molecules possessing lone pair of electrons (like H_2O, NH_3, en, gly, etc.). In neutral ligands, the most electonegative atom points towards the central metal ion.
3. Both metal ions and ligands act as point charges. The interaction between the electrons of the metal and the ligands is purely electrostatic.
4. When the ligands approach central metal atom, the electrons of central metal atom and those of ligands repel each other. These repulsive forces destroy the degeneracy of *d*-orbitals and split them into two groups called t_{2g} and e_g groups. The effect is called *crystal field splitting*.

   The crystal field splitting depends upon the geometry of the complex. This is because *d*-orbitals differ in orientation. The *d*-orbitals lying in the direction of ligands are affected to larger extent while those lying in between the ligands are less affected. Thus, due to repulsion, the orbitals along the axes of ligands acquire higher energy while the orbitals lying in between the ligands acquire lesser energy due to lesser repulsion. Therefore, on the approach of ligands, we have two sets of *d*-orbitals (of central metal) having different energies. The difference in the energy between these two sets is called **crystal field splitting energy** and is represented by Δ. This is often measured in terms of an arbitrary parameter Dq and the magnitude of the splitting energy is arbitrarily taken as $10Dq$, *i.e.,*

   $$\Delta = 10Dq$$

   The exact amount of splitting energy (Δ or $10Dq$) depends upon the geometry of the complex.
5. The electrons of the metal atom occupy splitted *d*-orbitals strictly in accordance to Hund's rule. The electrons first occupy those *d*-orbitals which suffer less repulsion, *i.e.,* the orbitals which have their lobes farthest away from the direction of ligands.
6. The theory does not take into account any overlapping between the orbitals of central metal atom and those of ligands. Hence, the theory totally rules out the possibility of any covalent character in the complex.
7. The stability of a complex can quantitatively be known by the magnitude of **crystal field stabilisation energy (CFSE).** The magnitude of CFSE depends upon the nature and number of ligands and also upon the geometry of the complex.

Q.3. Describe the use of CFT or give crystal field stabilizing energy (CFSE) in octahedral complexes.

Ans.

Application of Crystal Field Theory

In Octahedral Complexes

In an octahedral complex, six ligands occupy their positions at the six vertices of a regular octahedron with metal atom at the centre of the octahedron as shown in Fig. 1. Among the five *d*-orbitals, $d_{x^2-y^2}$ and d_{z^2} are axial orbitals and have maximum electron density along the axes, whereas, the remaining three *d*-orbitals (*i.e.*, *dxy, dyz* and *dzx*) are planar orbitals and possess maximum electron density in planes.

From Fig. 1, it is clear that in an octahedral complex, the axial orbitals, *i.e.*, $d_{x^2-y^2}$ and d_{z^2} are face to face to ligands which are situated at the vertices where as *dxy, dyz* and *dzx* orbitals lie in between the metal-ligand bond axes. Therefore, $d_{x^2-y^2}$ and d_{z^2} orbitals experience the maximum repulsion by the ligands while *dxy, dyz* and *dzx* orbitals are less affected. As a result, the energy of $d_{x^2-y^2}$ and d_{z^2} orbitals is increased much more as compared to the remaining three *d*-orbitals. Thus, the five degenerate *d*-orbitals lose their degneracy and split into two point group – t_{2g} and t_g. t_{2g} group of orbitals contain three degenerate *dxy, dyz* and *dzx* orbitals, whereas e_g group of orbitals contain two degenerate $d_{x^2-y^2}$ and d_{z^2} orbitals. Due to face to face repulsion, e_g group of orbitals possess higher energy than those of t_{2g} orbitals. The energy gap (crystal field splitting) in betwen these two sets is Δ_0 or $10Dq$ (the subscript *o* in Δ_0 refers to octahedral geometry).

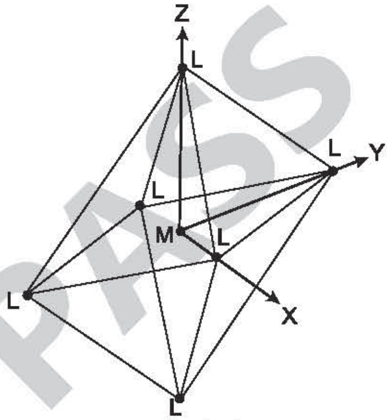


Fig. 1 : Octahedral geometry having central meal (*M*) at the centre and six ligands (L) at the vertices of the octahedron.

The crystal field splitting in case of an octahedral complex is shown in Fig. 2.

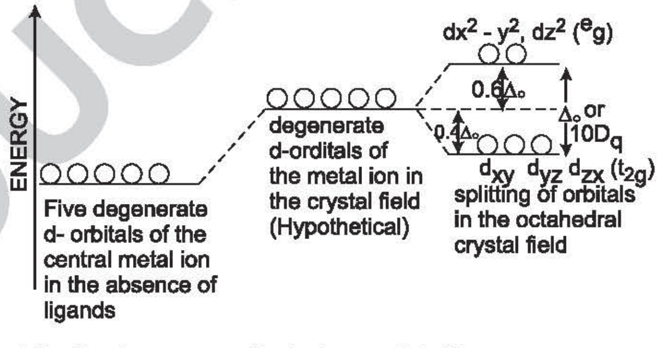


Fig. 2 : Splitting of *d*-orbitals in an octahedral crystal field. Here $\Delta_0 = 10Dq$, $0.6\,\Delta_0 = 6Dq$ and $0.4\,\Delta_0 = 4Dq$.

Calculations have shown that in this case, the energy of the t_{2g} orbitals is less by an amount $0.4\Delta_0$ or $4Dq$ as compared to the energy of hypothetical degenerate *d*-orbitals in crsytal field while those of e_g orbitals is more by an amount $0.6\Delta_0$ or $6Dq$ than those of hypothetical degenerate *d*-orbitals in crystal field. Calculations have also shown that each electron entering into t_{2g} orbital stabilises the complex by $0.4\Delta_0$ or $4Dq$ while each electron entering into e_g orbital destabilises the complex by $0.6\Delta_0$ or $6Dq$. The total gain of energy obtained by filling the electrons in *d*-orbitals gives the crystal field stabilisation energy (CFSE). The stability of the complex depends upon this energy.

The magnitude of Δ_0 or $10Dq$ depends upon the strength of ligands. When ligand field is strong, the splitting is large and consequently the value of Δ_0 is high. In case of a weak ligand field, the splitting is comparatively less and consequently the value of Δ_0 is also less. Therefore, the filling of electrons in *d*-shell depends upon whether the ligand field is strong or weak.

Ligands can be arranged in a series in the order of increasing field strength as given below.

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$$

Such a series is termed as **spectrochemical series.** It is an experimental series and is based upon the absorption of light by complexes with different ligands.

Filling up of Electrons in *d*-Orbitals

The electrons get filled up in the splitted d-orbitals in accordance to the following rules :

1. Electrons fill up the splitted d-orbitals strictly in accordance to Hund's rule of maximum multiplicity, *i.e.,* electrons prefer to occupy vacant orbitals of lower energy.
2. In case of a strong ligand field, when Δ_0 $(10Dq)$ is large and greater than the pairing energy *P* (the energy required by the electrons to get paired up), *i.e.,* $10Dq > P$, electrons get paired up in low energy t_{2g} orbitals instead of going to higher energy t_g orbitals. The complex thus obtained contains a majority of paired electrons and possesses low spin. Such a complex is called a **low spin complex.**
3. In case of a weak ligand field Δ_0 $(10Dq)$ is small and less than the pairing energy P, *i.e.*, $10Dq < P$. The electrons thus prefer to go to higher energy e_g levels and tend to remain unpaired as far as possible. The complex thus obtained may possess high spin and is called a high spin complex.

   (i) **Arrangement of electrons in a strong ligand field (Low spin octahedral complexes) :** The strong ligands such as CO, CN^-, NO_2, en, NH_2^- etc., cause large splitting of *d*-orbitals. Therefore, the values of Δ_0 or $10Dq$ is greater than that of pairing energy P, *i.e.*, Δ_0 $(10Dq) > P$. Thus, the electrons prefer to get paired up in lower t_{2g} orbitals instead of going to higher e_g orbitals.

   In octahedral complexes with d^1 configuration, the only *d* electron occupies t_{2g} orbital and stabilises the complex by $-0.4\ \Delta_o$ or $-4Dq$. The CFSE in this case would thus be $-4Dq$. Similarly in complexes with d^2 and d^3 configurations, the electrons will occupy t_{2g} orbitals and will remain unpaired. The CFSE in these cases would respectively be $-8Dq$ and $-12Dq$. In the octahedral complex with d^4 configuration, the fourth electron can not go to e_g orbital because $10Dq$ is large and is greater than *P*. Hence, this electron has to be paired up in one of the t_{2g} orbitals. The CFSE in this case would be

$$\text{CFSE} = 4 \times (-4Dq) + 1 \times P = -16Dq + P$$

Similar is the situation with octahedral complexes with configuration d^5 and d^6. The fifth and sixth electrons in these complexes will also get paired up in t_{2g} orbitals. The CFSE in these cases will be $-20Dq+2P$ and $-24Dq+3P$ respectively.

Table 1 : Arrangement of Electrons in Octahedral Complexes and Corresponding CFSE in Strong Ligand Field

No. of *d* electrons in the metal ion	Low energy t_{2g} orbitals			High energy e_g orbitals		No. of unpaired electrons	CFSE
d^1	↑					1	$-4Dq$
d^2	↑	↑				2	$-8Dq$
d^3	↑	↑	↑			3	$-12Dq$
d^4	↑↓	↑	↑			2	$-16Dq+P$
d^5	↑↓	↑↓	↑			1	$-20Dq+2P$
d^6	↑↓	↑↓	↑↓			0	$-24Dq+3P$
d^7	↑↓	↑↓	↑↓	↑		1	$-18Dq+3P$
d^8	↑↓	↑↓	↑↓	↑	↑	2	$-12Dq+3P$
d^9	↑↓	↑↓	↑↓	↑↓	↑	1	$-6Dq+4P$
d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	0	$0\,Dq+5P$

In octahedral complexes with d^7 configuration, the seventh electron has no other way than to go to a higher energy e_g orbital. This electron destabilises the complex by 6 *Dq*. Therefore, the CFSE in this case would be

$$\text{CFSE}=6\times(-4Dq)+(1\times 6Dq)+3P=-18Dq+3P$$

This type of complexes contain only one unpaired electron. In the same way octahedral complexes with d^8, d^9 and d^{10} configurations would have CFSE equal to $-12Dq+3P, -6Dq+4P$, and $0\,Dq+5P$ respectively. The arrangement of electrons in all possible type of octahedral complexes, corresponding CFSE and number of unpaired electrons possessed by them are shown in Table 2.

(ii) **Arrangement of electrons in a weak ligand field (High spin octahedral complexes) :** Weak ligands like $H_2O, OH^-, Cl^-, Br^-, I^-$ etc., cause only a very small splitting of *d*-orbitals. Therefore, the value of Δ_0 or 10 *Dq* is small and much less than the pairing energy *P, i.e.,* 10 *Dq* < *P*. Therefore, in this case electrons prefer to go to high energy e_g orbitals instead of getting paired up in low energy t_{2g} orbitals.

The octahedral complexes with d^1, d^2 and d^3 configurations have the same distribution of electrons as in case of strong ligand field. The configuration of complexes with d^4 are different. Now the fourth electron goes to e_g orbital and remains unpaired. Therefore, a d^4 complex possesses four unpaired electrons in a weak ligand field. The CFSE of a d^4 complex would thus be

$$\text{CFSE}=3\times(-4Dq)+(1\times 6Dq)=-6Dq.$$

Similarly in case of d^5 complexes, the fifth electron will also remain unpaired in e_g orbital and the complex will contain five unpaired electrons. The CFSE can be calculated in the same way and comes out to be equal to

$$\text{CFSE} = 3 \times (-4Dq) + (2 \times 6Dq) = 0\ Dq.$$

In case of d^6 octahedral complexes, the sixth electron has no other option than to get paired up in one of t_{2g} orbitals. This type of complexes will thus have four unpaired electrons with CFSE equal to

$$\text{CFSE} = 4 \times (-4Dq) + (2 \times 6Dq) + P = -4Dq + P.$$

The configuration of d^7, d^8, d^9 and d^{10} type octahedral complexes can be obtained similarly. The electronic arrangements in all possible types of octahedral complexes in weak ligand field with corresponding CFSE and number of unpaired electrons have been shown in Table 2.

Table 2 : Arrangement of Electrons in Octahedral Complexes and Corresponding CFSE in Weak Ligand Field

No. of *d* electrons in the metal ion	Low energy t_{2g} orbitals			High energy e_g orbitals		No. of unpaired electrons	CFSE
d^1	↑					1	$-4Dq$
d^2	↑	↑				2	$-8Dq$
d^3	↑	↑	↑			3	$-12Dq$
d^4	↑	↑	↑	↑		4	$-6Dq$
d^5	↑	↑	↑	↑	↑	5	$0Dq$
d^6	↑↓	↑	↑	↑	↑	4	$-4Dq + P$
d^7	↑↓	↑↓	↑	↑	↑	3	$-8Dq + 2P$
d^8	↑↓	↑↓	↑↓	↑	↑	2	$-12Dq + 3P$
d^9	↑↓	↑↓	↑↓	↑↓	↑	1	$-6Dq + 4P$
d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	0	$0\ Dq + 5P$

Q.4. Describe the use of CFT or give crystal field stabilizing energy (CFSE) in tetrahedral complexes.

Ans.

Application of CFT in Tetrahedral Complexes

In a tetrahedral complex, the four ligands are placed at the four corners of a regular tetrahedron while the metal is placed at the centre of tetrahedron as shown in Fig. 3.

From the geometry of the complex, it is clear that ligands approach the central metal atom in between the three coordinate axes. Therefore, the orbitals *dxy, dyz, dzx* (t_{2g} orbitals) lying in different planes are now pointed

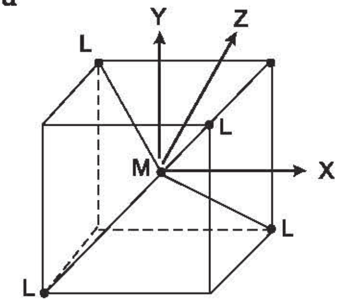


Fig. 3 : Tetrahedral geometry having central metal atom (*M*) at the centre and four ligands (*L*) at the four corners.

towards ligands while the axial orbitals $dx^2 - y^2$ and dz^2 (e_g orbitals) lie in between the metal- ligand bond axes. Hence, t_{2g} orbitals experience much more repulsion by the ligands as compared to that experienced by e_g orbitals. Due to greater repulsion, the *dxy, dyz* and *dzx* orbitals are now of higher energy while $dx^2 - y^2$ and dz^2 orbitals are of comparatively lower energy. Moreover, since the orbitals do not interact directly with the ligand orbitals, the splitting of *d* levels is much less as compared to octahedral ligand field splitting.

The crystal field splitting of d-orbitals in a tetrahedral ligand field is shown in Fig. 4.

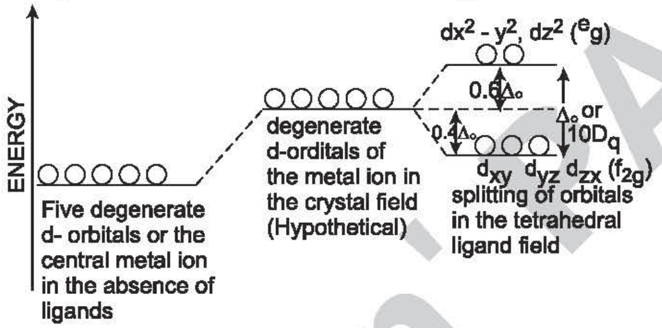


Fig. 4 : Splitting of *d*-orbitals in a tetrahedral crystal field.
Here $\Delta_t = 10Dq, 0.4\Delta_t = 4Dq$ and $-.6\Delta_t = 6Dq$

Calculations have shown that t_{2g} orbitals are raised by $4Dq$ whereas e_g orbitals are lowered by $6Dq$ as compared to the energy of hypothetical degenerate *d*-orbitals in ligand field. The energy gap, *i.e.,* the crystal field splitting between the two sets is Δ_t, or $10Dq$ (the subscript *t* in Δ_t, refers to tetrahedral geometry).

Calculations have also shown that each electron entering into low energy e_g orbitals stabilises the complex by $6Dq$, whereas each electron entering into high energy t_{2g} orbitals destabilises it by $4Dq$.

The distribution of electrons in these orbitals depends on whether the ligand field is strong or weak. In a strong ligand field, electrons prefer to get paired up in low energy e_g orbitals in place of going to high energy t_{2g} orbitals. Thus, we shall have a **low spin complex**. But if the ligand field is weak, the electrons would like to go to high energy t_{2g} orbitals in place of being paired up in low energy e_g orbitals and we shall have a **high spin complex**.

Colour in Coordination Compounds

Coordination compounds exhibit a wide range of colours. The sensation of colour is produced when light having a wavelength within the visible region (400 nm-750 nm) of electromagnetic spectrum strikes the retina of the eye. A complex shows colour when the white light passing through it is partly absorbed and partly reflected. The colour shown by the complex is the **complementary colour** generated from the wavelengths present in the partly reflected light. For example, if complex absorbs green light, it shows red colour. The relationship between the wavelength of the light absorbed and the colour shown by some complexes is given in Table 3.

Table 3 : Relationship Between the Wavelength of Light Absorbed and the Colour Shown by Some Complexes

Complex species	Wavelength of Light Absorbed	Colour of the Light Absorbed	Complementary Colour shown by the Complex Species
$[Co(CN)_6]^{3-}$	310 nm	Ultraviolet	Pale yellow
$[Co(NH_3)_6]^{3+}$	475 nm	Blue	Yellow orange
$[Ti(H_2O)_6]^{3+}$	498 nm	Yellow Green	Purple
$[Co(NH_3)_5(H_2O)]^{3+}$	500 nm	Blue green	Red
$[CoCl(NH_3)_5]^{2+}$	535 nm	Yellow	Violet
$[Co(H_2O)_4]^{2+}$	600 nm	Red	Blue

The colour shown by a complex can easily be explained on the basis of crystal field theory. According to the crystal field theory, colour of complexes is due to ***d-d* transitions** of electrons. For example, the violet colour of $[Ti(H_2O)_6]^{3+}$ can be explained as follows.

$[Ti(H_2O)_6]^{3+}$ is an octahedral complex. The central metal ion Ti^{3+} constitutes a $3d^1$ system. The only electron present in the $3d$-subshell lies in the t_{2g} level in the ground state of the complex. The next higher state available is empty e_g level. When the complex absorbs light from the yellow green region, the-electron present in the lower t_{2g} level gets excited to the higher e_g level. Thus, a *d-d* transition takes place as shown in Fig. 5.

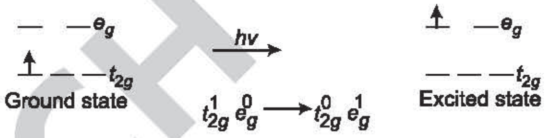


Fig. 5 : *d-d* transition in $[Ti(H_2O)_6]^{3+}$.

On account of this transition, the complex appears violet in colour.

In the absence of ligands, there is no crystal field splitting and hence the substance is colourless. For example, if water is removed from $[Ti(H_2O)_6]^{3+}$ by heating, it becomes colourless. Similarly $CuSO_4 \cdot 5H_2O$ is blue in colour, whereas anhydrous $CuSO_4$ is white.

Q.5. Describe the CFSE in squre planer complexes.

Ans.

CFT for the Square Planar Complex

CFT of the square planar complexes is arises from the CFT of octahedral complexes. The crystal field splitting diagram for the square planer complexes originated from the splitting diagram of octahedral complexes in the two steps which can be represented as :

If the two trans ligands in an octahedral ML_6 complex (consider those along the z-axis) are moved either towards or away from the metal ion, the resulting structure is said to be tetragonally distorted. Ordinarily such distortions are not favored since they result in a net loss of bonding energy. In certain situations, however, such a distortion is favored because of a **Jahn-Teller effect**. A complex of general formula *trans*-Ma_2b_4 also will have tetragonal symmetry. For now, we will consider the limiting case of tetragonal elongation, a square planar ML_4 complex, for the purpose of deriving its d-orbital splitting pattern. The crystal field diagram for the tetragonally distorted complex and the square-planar complexes is shown below. Removal of ligands from *z*-direction completely leads to the square-planar geometry (Fig. 6). This geometry is favoured by metal ions having a d^8 configuration in the presence of a strong field. This combination gives low-spin complexes where the first four orbitals are occupied and the high-energy $d_{x^2-y^2}$ orbital is unoccupied.

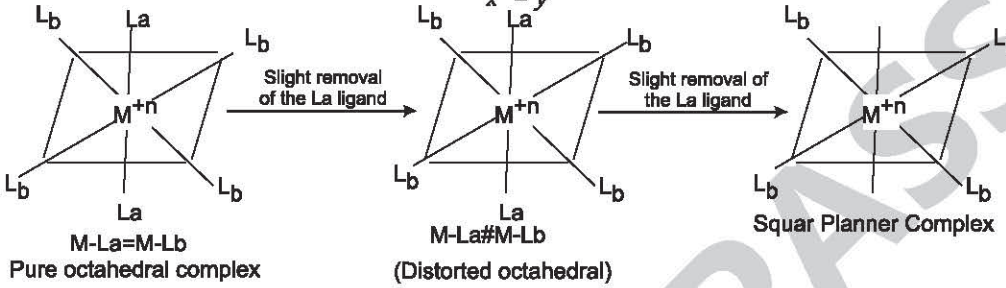


Fig. 6 : Formation of square planar complex from octahedral complex

Crystal Field splitting for square planar complex

Square planar complexes are similar to the octahedral complexes. The difference is that square planar complexes have two ligands missing in the *z*-axis. There is a very large energy gap between the $d_{x^2-y^2}$ orbital and the lower four orbitals. Square planar complexes are favored by metal ions with d^8 electron configurations. Since this configuration favours low spin complexes in which the four lower-energy orbitals are filled and the high energy $d_{x^2-y^2}$ orbital is empty. The crystal field splitting diagrame of square planar complex is given in Fig. 7.

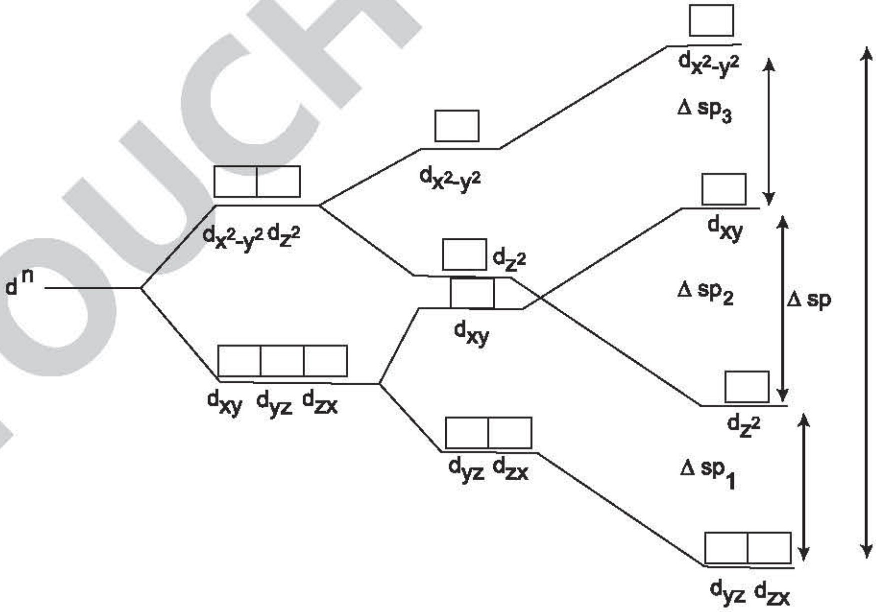


Fig. 7 : Crystal field splitting diagrame of square planar complex

Q.6. (i) What is John teller effect?

(ii) Write the factors affecting the crystal-field parameters.

Ans. (i) John Teller Effect

Hermann John and Edward Teller in 1937 offered a theorem that stated;

"A non-linear molecular system in an electronic degenerate state will undergo distortion that will remove the degeneracy, lower the symmetry and hence lower the overall energy".

This distortion is known as Jahn-Teller distortion (JTD) and the effect is called the Jahn-Teller effect (ITE). The John-Teller effect is one that lowers the symmetry in certain geometries, in order to bring the molecules into a more stable, lower energy state. This effect is associated with certain types of (*d*-orbital containing) electronic configurations only. The affected geometries include tetrahedral and most commonly, octahedral.

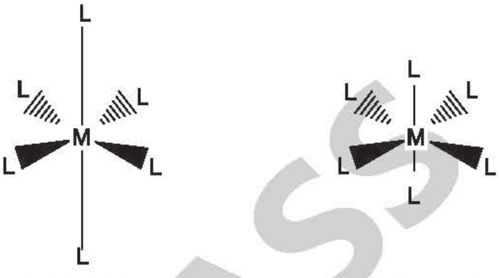


Fig. 8

In octahedral geometry, the types of distortions that occur are tetragonal elongation and compression which involve the movement of ligands on the *z*-axis. However, the inversion center is still preserved after the distortion (both the ligands on the z-axis are still equidistant from the center).

$$t_{2g} \text{ orbitals} = d_{xy}, d_{yz}, d_{xz}$$
$$e_g \text{ orbitals} = d_{x^2-y^2}, d_{z^2}$$

A non-linear molecular system in an electronic degenerate state refers to the uneven distribution of electrons in the *d*-orbitals, especially the e_g set of orbitals ($d_{x^2-y^2}$ and d_{z^2}). This is because the e_g set of orbitals is more affected (force of repulsion) by the ligands in the octahedral geometry, as the ligands approach the central metal atom on its axes (and not in between the axes, as in the t_{2g} set of orbitals).

John-Teller Effect

Number of electrons	High spin/Low spin	Strength of John-Teller effect
1.	—	Weak
2.	—	Weak
3.	—	—
4.	High spin	Strong
	Low spin	Weak
5.	High spin	—
	Low spin	Weak
6.	High spin	Weak
	Low spin	—
7.	High spin	Weak
	Low spin	Strong
8.	—	—
9.	—	Strong
10.	—	—

The John-Teller effect is most obvious in octahedrally coordinated metal ions with (high-spin) d^4, (low spin) d^7, and d^9 electronic configurations, all of which leave an unpaired electron in either of the e_g orbitals. The John-Teller theorem, however, does not explain the direction of distortion (tetragonal compression or elongation); it only signifies that distortion will occur, to lift the degeneracy and lower the energy.

When tetragonal compression or elongation takes place in an octahedral geometry, usually one of the orbitals in the e_g set ($d_{x^2-y^2}$ or d_{z^2} is half-filled. However, it is the tetragonal elongation that is the more common distortion of octahedral geometry.

(ii) Factors Affecting the Crystal Field Parameter

Some factors which can affect the value of Δ (Crystal field splitting energy difference) are given below :

1. Nature of ligands

With the increase in the strength of the ligands present in the complexes, the Δ value for the complexes is increases.

Explanation : With the increase in the strength of the ligand, the ability of the ligands to cause the closer approach with the central metal atom (CMA) increases by which the repulsion between the ligand and *d*-orbitals as well as Δ value also increases.

Examples :

1. $[Fe(CN)_6]^{-4}$ ion contains the stronger CN^- ligands while $[Fe(Cl)_6]^{-4}$ ion contains the weak Cl^- ligands due to which the Δ value for $[Fe(CN)_6]^{-4}$ ion is found to be more than $[Fe(Cl)_6]^{-4}$ ion.
2. $[Co(F)_6]^{-3}$ ion contains the stronger F^- ligand while $[Co(Cl)_6]^{-3}$ ion contains the weak Cl^- ligand due to which the Δ value for $[Co(Cl)_6]^{-3}$ ion is found to be less than $[Co(F)_6]^{-3}$ ion.

2. Nature of central metal atom (CMA)

1. **Same CMA with different charge :** If the complexes containing same CMA with the different charge, then the complex with the higher +ve charge of the CMA will exhibit higher Δ value.

   Explanation : In the complexes containing different charge on the CMA, the complex with the higher +ve charge of the CMA exhibit higher Δ value because the CMA with higher +ve charge can attract the ligand more closer toward itself by which the repulsion between the ligand and *d*-orbitals of CMA as well as Δ value is increases.
2. **Different CMA with the different charge :** If the complexes contain different charge, then the complex containing higher +ve charge on the CMA exhibit higher Δ value.

   Explanation : If the complexes contain different CMA with the different charge, then the complex containing higher +ve charge on CMA exhibit the higher Δ value because the CMA with the higher +ve charge can attract the ligand more closer toward itself due to which the repulsion between the ligand and *d*-orbitals of CMA as well as Δ value are increases.

Examples : (a) $[V(H_2O)_6]^{+2}$ complex ion contains lower +ve charge (+2) on the CMA while $[Cr(H_2O)_6]^{+3}$ ion contains higher + ve charge (+3) on the CMA due to which $[Cr(H_2O)_6]^{+3}$ ion will exhibit higher Δ value.

(b) $[Fe(NH_3)_6]^{+3}$ ion contains higher + ve charge of the CMA (+3) while $[Fe(NH_3)_6]^{+2}$ ion contains lower + ve charge of the CMA (+2) due to which $[Fe(NH_3)_6]^{+3}$ ion will exhibit higher Δ value.

(c) **Different CMA with same charge :** If the complexes contain different CMA with the same charge, then that complex containing lower d^n configuration of CMA will exhibit higher value.

Explanation : This can be due to shielding effect.

Example : $[Fe(H_2O)_6]^{+2}$ ion has $3d^6$ configuration of CMA while $[Co(H_2O)_6]^{+2}$ ion contains the $3d^7$ configuration of CMA and both these complexes have same charge value, thus, the former complex ion with lower d^n configuration will exhibit high Δ value.

(d) **Principal quantum no of d^n configuration :** With the increase in the Principal quantum number of d^n configuration of CMA, the value of Δ is increases. In other word the Δ value for the complexes of II-transition series elements being 30% greater than the Δ value for the complexes of I-transition series elements and the Δ value for the complexes of III-transition series element being greater than the II-transition series elements.

Example : $[Fe(CN)_6]^{-4}$ ion exhibits lower Δ value than the $[Ru(CN)_6]^{-4}$ ion because Ru have higher Principal quantum number of d^n configuration in comparison to Fe.

Q.7. (i) Describe the thermodynamics stability of metal complexes.

(ii) Write the factors affecting the stability of a complex.

Ans.

(i) Thermodynamic Stability of Metal Complexes

The thermodynamic stability of a complex depends upon the extent of interaction between the metal ion and ligands. If the interaction is strong, the complex formed would be thermodynamically more stable.

As we have seen earlier, the reaction between a metal ion and a ligand can be regarded as a Lewis-acid base reaction. Suppose a metal ion M^{a+} interacts with n ligands L^{x-} to form a complex $[ML_n]^{b+}$, where a, x and b represent the charges on the metal, ligand and complex respectively. The reaction between the metal ion and ligands can be described by the following equilibrium.

$$M^{a+} + nL^{x-} \rightleftharpoons [ML_n]^{b+}$$

The equilibrium constant for the above equilibrium is termed as the **stability constant** and is represented by K. It is given by

$$K = \frac{[ML_n]^{b+}}{[M^{a+}][L^{x-}]^n}$$

The stability constant is an important parameter of a complex. It may be used to express the thermodynamic stability of a complex because it gives an indication of the stability of the complex in solution. Higher the value of stability constant, greater is the thermodynamic stability of the complex in solution.

The values of stability constant (*K*) for some common complexes in solution are given below.

System	Stability constant (*K*)
$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3×10^{7}
$Ag^{+} + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^{+}$	1.6×10^{7}
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	4.5×10^{11}
$Ag^{+} + 2CN^{-} \rightleftharpoons [Ag(CN)_2]^{-}$	5.5×10^{18}
$Cu^{2+} + 4CN^{-} \rightleftharpoons [Cu(CN)_4]^{2-}$	2.0×10^{27}
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	5.0×10^{33}

The above values of stability constants indicate that the cyano complexes are more stable than the ammine complexes. Hence, it may be concluded that CN^{-} is a stronger ligand than NH_3.

(ii) Factors Affecting the Stability of a Complex

The thermodynamic stability of a complex depends upon the following factors.

1. **Charge density on the central metal ion :** The stability of a complex depends upon the charge density on the central metal ion which in turn depends upon the magnitude of charge and the radius of the ion, *i.e.,* charge/radius ratio. Higher the magnitude of charge and smaller the size of ion, more is the charge density on the ion and greater is the stability of the complex.

   For example, the magnitude of positive charge on Cu^{2+} and Cd^{2+} ions is the same but the ionic radius of Cu^{2+} ion (69 pm) is less than that of Cd^{2+} ion (97 pm). Obviously, the charge density on Cu^{2+} is greater than that on Cd^{2+} ion because the former has a higher charge/radius ratio. This is why complexes formed by Cu^{2+} ion are more stable than those formed by Cd^{2+} ion as is clear from the data given above (*K* for $[Cu(NH_3)_4]^{2+} = 4.5 \times 10^{11}$; *K* for $[Cd(NH_3)_4]^{2+} = 1.3 \times 10^{7}$).

   Ionic radii of some bivalent metal ions are given below.

Ion	Cu^{2+}	Ni^{2+}	Co^{2+}	Fe^{2+}	Mn^{2+}	Cd^{2+}
Ionic radius (pm)	69	78	82	83	91	97

   Therefore, with the same ligand, the stability of complexes formed by these ions follows the following order.

$$\underset{\xrightarrow{\text{Stability of complexes decreases}}}{Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Cd^{2+}}$$

2. **Nature of ligands :** Ligands are Lewis bases because they act as electron donors during the formation of a complex. Therefore, the stability of a complex should depend upon the ease with which the ligands donate lone pairs of electrons to the central metal

ion, *i.e.*, on the basic strength of the ligand. Hence, greater the basic strength of the ligand, greater is the stability of the complex.

For example, CN^- is more basic than NH_3. Therefore, cyano complexes of a metal ion are more stable than its ammine complexes as is evident from the following data :

$$K \text{ for } [Ag(CN)_2]^- = 5.5\times10^{18}; K \text{ for } [Ag(NH_3)_2]^+ = 1.6\times10^{7}$$

Q.8. Describe the Pearson's HSAB concept in detail.

Ans.

Pearson's HSAB Concept : Acid Base Strength and Hardness and Softness

According to the Pearson HSAB concept, hard acid-hard base combination & soft acid-soft base combination give rise to the more stable compound or complexes in comparision to the hard acid-soft base & soft acid-hard base combination compound.

$$\text{Hard acid + hard base} \rightarrow \text{more stable compound/complexes}$$

$$\text{Soft acid + soft base} \rightarrow \text{more stable compound/complexes}$$

Or

$$\left.\begin{array}{l}\text{Hard acid + soft base}\\ \text{Soft acid + hard base}\end{array}\right\}\longrightarrow \text{Less stable complexes}$$

Explanation : Due to the very low polarise ability of hard acid and hard base their combination are ionic in nature while due to the very high polarize ability of soft acid and soft base their combinations are covalent in nature. Both these combinations of ionic and covalent nature have more stable combination due to which HSAB principle states the hard hard and soft-soft combinations as a stable combination.

Applications of HSAB principle

Occurrence of metal ions on the earth : Lighter metal ions like $Li^+, Na^+, Mg^{+2}, Ca^{+2}$ etc. exist in the form of there chlorides, carbonates, sulphates, phosphates ($O^{-2}, CO_3^{-2}, SO_4^{-2}, PO_4^{-3}$) on the earth crust but cannot exist in the form of their sulphides (S^{-2}) while on the other hand heavier metal ions like Ag^+, Hg^+, Cu^+ etc. exist in the form of their sulphides on the earth crust and cannot exist in the form of $CO_3^{-2}, O^{-2}, SO_4^{-2}$ etc.

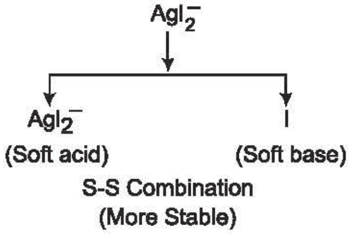
Explanation : Lighter metal ions like $Li^+, Na^+, K^+, Mg^{+2}, Al^{+3}$, etc. form the stable hand-hand combination with the $O^{-2}, CO_3^{-2}, SO_4^{-2}, PO_4^{-3}$ on the earth crust due to which they exist in the form of their oxides, carbonate, sulphates and phosphates while these lighter metal ion forms the less stable unstable hard soft combination with the sulphide ion due to which they connot exist in the form of there sulphides on the earth crust. Heavier metal ion like Ag^+, Hg^+, Cu^+ etc. form the stable soft-soft combination with the S^{-2} ion due to which they can exist in the form of their sulphides on the earth crust while on the other hand, the heavier metal ion like Ag^+, Hg^+, Cu^+ etc. form the unstable or less stable soft-hard combination with the $O^{-2}, CO_3^{-2}, SO_4^{-2}, PO_4^{-3}$ etc. due to which they cannot exist in the form of there oxides, carbonates, sulphates and phosphates on the earth crust.

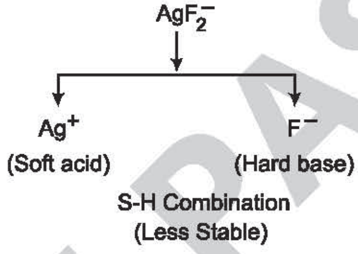
Stability of the compound/complexes

With the help of HSAB principle, we can compare the stability of various compounds or complexes.

1. AgI_2^- is more stable than the AgF_2^-.

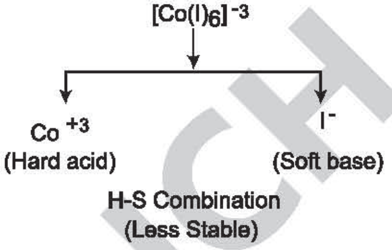
   Explanation : AgI_2^- containing soft-soft combination due to which accoding to the HSAB principle, AgI_2^- well be more stable while AgF_2^- containing soft-hard combination, will be less stable or sometime cannot exist.

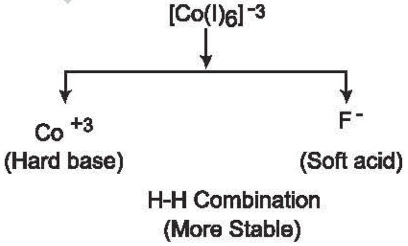




2. $[Co(F)_6]^{-3}$ is being more stable then $[Co(I)_6]^{-3}$ ion.

   Explanation : $[Co(F)_6]^{-3}$ ion containing hard-hard (H-H) combination is more stable while on the other hand, $[Co(I)_6]^{-3}$ ion having hard-soft (H-S) combination, will be less stable.





Stability of the complexes containing different ligand

According to the Pearson principle, a complex containing more than one type of the ligands (hard or soft), then the complex will be more stable.

$[Co(N)_5(F)]^{-3}$ ion is less stable than $[Co(CN)_5(I)]^{-3}$ ion.

Explanation : $[Co(N)_5(F)]^{-3}$ ion containing soft CN^- & Hard F^- ligands will be less stable while on the other hand $[Co(N)_5(I)]^{-3}$ ion containing both the soft ligands (CN^- and I^-) will be more stable.

Occurrence of the chemical reaction

With the help of HSAB principle we can give the idea about the occurrence of the chemical reaction. According to HSAB principle, if the reactants present in the chemical reaction have less stable H-S & S-H combinations, then they will have the tendency to react with each other to generate the more stable H-H & S-S combinations i.e. in such condition chemical reaction will be possible. If the reactants have more stable H-H & S-S combinations, then they will not have the tendency to convert into the less stable H-S & S-H combinations by the reaction *i.e.,* in such condition reaction will not be possible.

$$\underset{(H\text{-}S)}{Li} + \underset{(S\text{-}H)}{CsF} \longrightarrow \underset{(H\text{-}H)}{LiF} + \underset{(S\text{-}S)}{CsI}$$

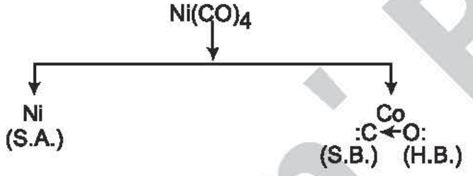
In the above reaction, both the reactants have less stable H-S & S-H combinations and the products have the more stable H-H & S-S combination so acc to HSAB principle the above Reaction will be possible.

$$\underset{(H\text{-}H)}{BeF_2} + \underset{(S\text{-}S)}{HgI_2} \longrightarrow \underset{(H\text{-}S)}{BeI_2} + \underset{(S\text{-}H)}{HgF_2}$$

In the above reaction, both the reactants have more stable (H-H, S-S) combinations and products haveless stable H-S and S-H combinations. Hence, according to HSAB principle, this reaction will not be possible.

Nature of the doner site in the ambident ligand

With the help of HSAB principle, we can also give an idea about the actual doner site of an ambident ligand.



When the C atom of the CO behave as a doner site, then there occur the formation of more stable S-S combination with the central metal atom (Ni) while when the O atom of CO behaves as a doner site, then there occur the formation a less stable S-H combination with the central metal atom (Ni). Therefore, the actual doner site of CO will be carbon.

Limitation of HSAB principle

According to HSAB concept, chemical reactions have a tendency to occur in such direction which can generate the more stable H-H & S-S combination. But sometimes the chemical reactions can also occur in such direction which can generate the less stable S-H & H-S combination and this can not be explained by HSAB concept of Pearson.

Q.9. (i) Describe the trans effect in the square planar complexes.

(ii) Describe nucleophilic substitution reactions of square planar complexes.

Ans.

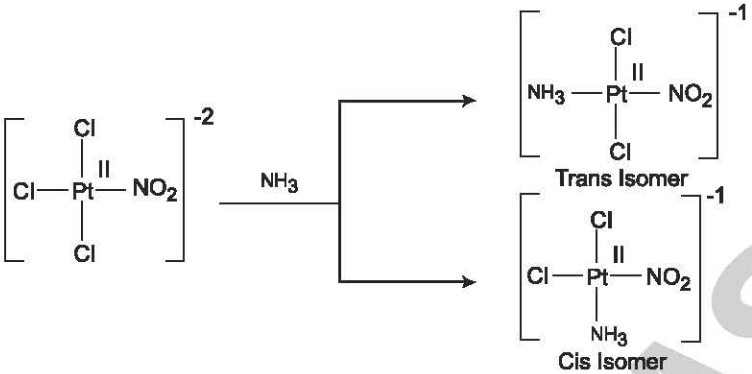
Trans Effect in the Square Planar Complexes

Ability of any particular ligand to replace the ligand present in the trans position by any other ligand in the Pt (II) square planar complexes is known as it's trans effecting ability or power and this type of the replacement phenomena is called as trans effect.

Different ligands having the different trans effecting power. When we arrange the various ligands in order of their increasing trans effecting power, then the arrangement which is obtained is called as trans effecting series. Arrangement of certain ligands in order of their increasing trans effecting power in trans effecting series can be given as :

$$CN^-, NO, CO, C_2H_4 > PR_3 > NH_2—CO—NH_2 > NO_2^-, I^-, SCN^- < Br^- > Cl^-$$
$$> F^- > Py, NH_3 > H_2O, OH^-$$

Example : When $[Pt(Cl)_3(NO_2)]^{-2}$ complexes ion react with NH_3 ligand, then two types of the isomeric forms of $[Pt(Cl)_2(NO_2)]^{-1}$ can be expected which are given below :



But experimentally, it was observed that only trans isomer is formed which can be due to the more trans effecting power of NO_2 than the Cl^- ion.

Theories of the trans effect phenomena : Trans effect phenomena in the Pt (II) square planar complexes can be explained by the two different types of the concepts :

1. **Polarisability concept :** According to the polarisability concept, if the Pt(II) square planar complexes contain two different ligands in the trans position, then the ligand with the high polorisability exhibits more trans effecting power because this ligand due to its more polarbility, increases the strength of bond with the CMA and removal of trans ligand become easier.
2. **π-bonding concept :** If the square planar complexes have non π-bonding and π-bonding ligands in trans position with each other, then the π-bonding ligand exhibits more trans effecting power because the π-bonding ligand increases the strength of bonding with the CMA and thus, removal of the non π-bonding ligand present trans to it become easier.

(ii) Nucleophilic Substitution Reactions of Square Planar Complexes

Before starting the study on mechanism of ligand substitution reactions in coordination compounds the following terms should be defined.

Transition state or activated complex

Let us consider the energy changes occurring during the course of the reaction.

$$\underbrace{X—Y—Z}_{\text{Reactants}} \longrightarrow \underbrace{X—Y + Z}_{\text{Product}}$$

Fig. 9

Initially, both *X* and *Y-Z* posses certain amount of potential energy represented by the point (a) on the curve, increase in the potential energy occur until a critical energy state (in which *Y-Z* bond is weakened at point b) and ultimately the products, *X-Y* and *Z* are formed as shown at point (c) (Figure 9). In this process, the potential energy of the system is again changed into kinetic energy and then into heat or any other form of energy. Figure 9 (a) illustrates that for an exothermic reaction, the reactants originally posses more potential energy than the products and excess energy (+Δ*H*) is liberated as heat. Figure 9 (b) shows that for an endothermic reaction, the reactants have less potential energy than the products and, therefore, the reactants absorb heat equal to *H* from the surroundings during their change into products. The energy difference between the reactants and the products is Δ*H* and is called reaction energy.

The reaction, $X + Y—Z \longrightarrow X—Y + Z$

The above reaction can take place by the following steps :

The molecule *X* approaches *Y-Z* from a direction remote from *Z*. While *X* draws nearer to *Y*, *Z* starts being repelled from *Y* until a stage is reached in which *X* and *Z* are rather loosely attached to *Y* and approximately equidistant from it. In this stage, the species *X...Y...Z* is formed. This species is called the transition state or activated complex which has the following characteristics.

1. In this *X* to *Y* and *Y* to *Z* distances are slightly greater than the normal bond lengths.
2. It is not a true molecule as the bonds are partial. Thus, it is of a transitory nature and refers to an imaginary molecule and hence cannot be isolated.
3. It has the maximum energy and hence, is the most unstable and has very-very short life time. The activated complex which is the most unstable state, changes to give the products *X-Y* and *Z*. The various steps responsible for the reaction are :

$$\underset{\text{Reactants}}{X + Y—Z} \longrightarrow \underset{\text{Activated complex}}{X\text{---}Y\text{---}Z} \longrightarrow \underset{\text{Product}}{X—Y + Z}$$

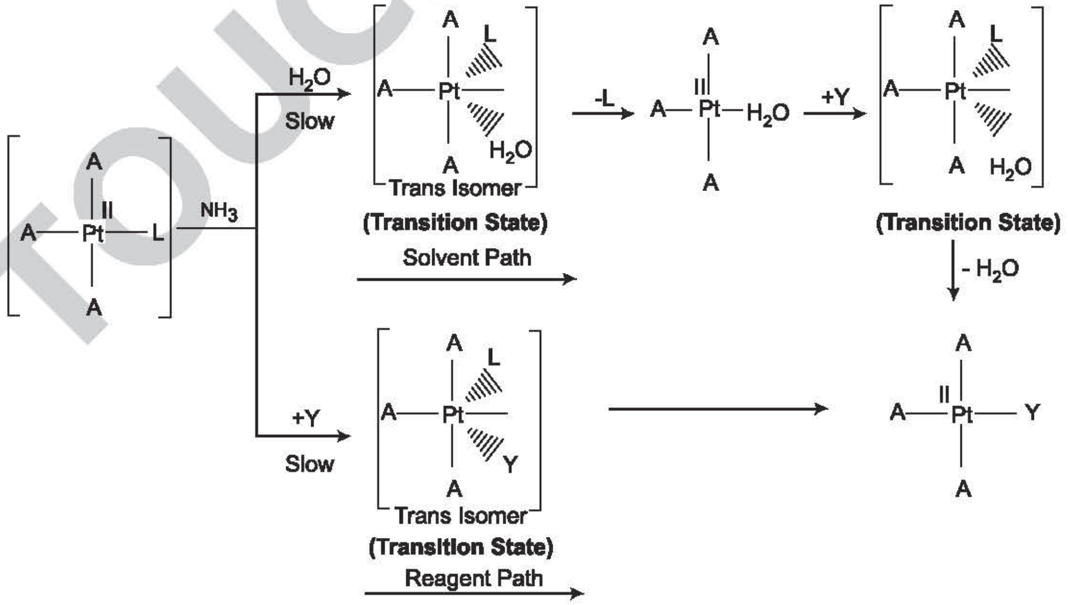
The difference in energy between the reactants and the activated complex is called activation energy.

Q.10. Describe electrophilic substitution reaction of square planar complexes.

Ans.

Nucleophilic substitution reactions (S_N2) in square Planar Complexes

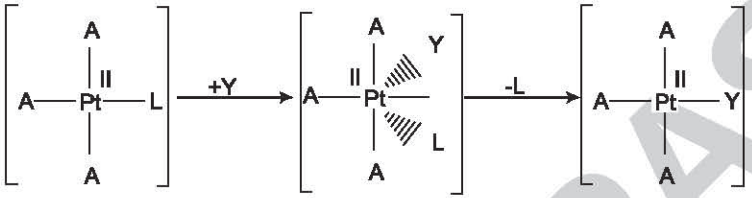
When the Pt (II) square planar complexes undergo nucleophilic substitution reaction with the various ligands, then the reaction occurs by the S_N2 mechanism through two different paths, which are known as solvent path and reagent path. Nucleophlic substitution reaction in the $[Pt^{II}A_3L]$ square planar complex by the S_N2 mechanism takes place through both the solvent path & reagent path which can be represented as :



Factors affecting the S_N2 reaction of square Planar Complexes

Some of the factors which can affect the rate of the S_N2 reaction in the square planar complexes are given below :

1. **Trans Effect :** In the Pt(II) square planar complexes, with the increase in the trans effecting power of ligand (A) present in the trans position of leaving ligand (L), the rate of S_N2 reaction increases.

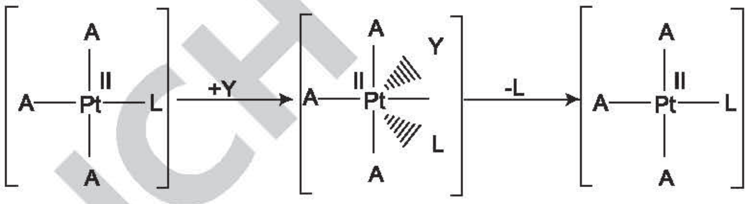


   Where $A = C_2H_4, NO^{2-}, Br^-, Cl^-; L = F^-$

   Trans effecting power of $A = C_2H_4 > NO^{2-} > Br^- > Cl^-$

   Rate of S_N2 reaction $= C_2H_4 > NO^{2-} > Br^- > Cl^-$

2. **Nature of leaving ligand (L) :** With the increase the trans effecting power of leaving ligand (L), it's bonding with CMA become more and more stable by which it's rate of replacement decreases. **Example :**



   Where $A = C_2H_4 ; L = PR_3, NO_2^-, Br^-, Cl^-, F^-$

   Trans effecting power of $L = PR_3 > NO_2^- > Br^- > Ci^- > F^-$

   Rate of S_N2 reaction $= PR_3 > NO_2^- > Br^- > Cl^- > F^-$

3. **Solvent Effect :** According to the kinetic evidence of S_N2 reaction, it was observed that S_N2 reaction can also be affected by the solvent.

UNIT-VIII

Inorganic Spectrocopy and Magnetism

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Write the ground state terms for the d^n ion.

Ans.

Configuration	Ground State Term
d^1, d^9	^2D
d^2, d^8	^3F
d^3, d^7	^4F
d^4, d^6	^5D
d^5	^6S

Q.2. Write the values of β_1, β_2 and β_n or overall formation constants.

Ans. $\beta_1 = \frac{[M_2]}{[M][L]}, \beta_2 = \frac{[ML_2]}{[M][L]^2}, \beta_n = \frac{[MLN]}{[M][L]^n}$

Q.3. Write the formula for magnetic permeability.

Ans. $p = \frac{B}{H}$

Q.4. Write the formula of magnetic susceptibility.

Ans. $x = \frac{I}{H}$

Q.5. Write the types of magnetism.

Ans. (i) Diamagnetism, (ii) Paramagnetism, (iii) Fermamagnetism, (iv) Antiferomagnetism, (v) Ferrimagnetism

Q.6. Write some examples of diamagnetic substances.

Ans. Cu^+, Zn^{2+}, Ga^+, etc.

Q.7. Write some examples of paramagnetic substances.

Ans. $Co^{2+}, Ni^{2+}, Cu^{2+}$, etc.

Q.8. Write some examples of ferromagnetic substances.

Ans. Fe, Co, Ni, etc.

Q.9. Write some examples of antiferromagnetic substances.

Ans. $Fe^{3+}, Mn^{2+}, Gd^{2+}$, etc.

Q.10. Write some examples of ferrimagnetic substances.

Ans. Fe_3O_4, etc.

Q.11. Write the types of electronic transitions.

Ans. 1. $\sigma \rightarrow \sigma^*$ transition.

2. $n \rightarrow \sigma^*$ transition.

3. $\pi \rightarrow \pi^*$ transition.

4. $n \rightarrow \pi^*$ transition.

Q.12. Write spin only formula.

Ans. $\mu_{\text{spin only}} = \sqrt{n(n+2)}$

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. Write the types of electronic transitions.

Ans.

Types of Electronic Tranisition

When the Electromagnetic Radiation (EMR) is passed from the sample of the transition metal complexes, the transition of electron can occur by the absorption of certain EMR to give the electronic spectra.

Electronic transitions can be classified into two different types, which are given below (Fig. 1) :

1. **Allowed transitions :** The types of electronic transition which can generate the high intense spectra are known as allowed transitions.
2. **Forbidden transitions :** The types of electronic transition which can generate the low intense spectra are known as forbidden transitions.

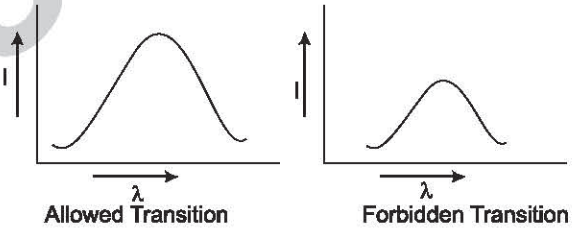


Fig. 1 : Types of *d-d* transition

Q.2. What is spectro chemical series?

Ans.

Spectrochemical Series

Order of ligands arranged according to the strength of ligand and arrangement of metal ions on the basis of oxidation number, group and its identity is called as spectrochemical series. According to crystal field theory, ligands can change the difference in energy between the two sets of *d*-orbitals (Δ_0) called the ligand-field splitting parameter for ligands or the crystal-field splitting parameter, which can be the cause of differences in color of similar type of metal ligand complexes.

The spectrochemical series was first given in 1938 and was based on the results of absorption spectra of cobalt complexes. Spectrochemical series of the ligands from smaller value of Δ_0 to larger value of Δ_0 is given below.

$O_2^{2-} < I^- < Br^- < S^{2-} < SCN^- < Cl^- < N^{3-} < F^- < NCO^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN$
< py (pyridine) < NH_3 < en (ethylenediamine) < bipy (2, 2'-bipyridine) < phen (1, 10-phenanthroline) < $NO_2^- < PPh_3 < CN^- \approx CO$

Ligands present on the left end of this spectrochemical series are generally known as weaker ligands and cannot cause pairing of electrons within 3*d* level and thus, form outer orbital octahedral complexes and are called as high spin ligands. While, ligands present at the right end of the series are stronger ligands which can form inner orbital octahedral complexes after forcible pairing of electrons within 3*d* level and hence, are called as low spin ligands.

The strong ligands in the spectrochemical series are also called as π-acceptor ligands while weak ligands are known as σ-donor ligands.

Q.3. What are paramagnetic substances?

Ans.

Paramagnetic substances

The substances which, when placed in magnetic field, allow the magnetic lines of force to pass through them rather than through vacuum, are called paramagnetic substances and the propety due to which they show this behaviour is called paramagnetism.

Paramagnetism is subdivided in to (i) normal paramagnetism (ii) temperature independent and (iii) Pauli or free electron paramagnetism.

Origin of paramagnetism : Paramagnetism of a substance consisting of atoms, ions or molecules is caused by the presence of unpaired electrons in the substance. The greater the number of unpaired electrons, the greater will be paramagnetism shown by the substance. Paramagnetic molecules are free to orient themselves ideally in the gas phase, but in practice, also in solution and even in the solid state, if magnetically dilute.

Q.4. What are diamagnetic substances?

Ans.

Diamagnetic substances

Substances which do not possess unpaired electrons (their electrons are paired), do not show any magnetic moment. Such substances are repelled by external magnetic field. This is because, the magnetic fields produced by paired electrons are neutralized and no net magnetic field is produced by them.

Origin of diamagnetism : If two electrons with opposite spins are paired in the same orbital, the magnetic field produced by one electron is cancelled by that caused by the other electron, because each of the two electrons has equal and opposite magnetic moment. Thus, the substances having ony paired electrons give zero resultant magnetic moment and consequently are diamagnetic.

Dimagnetic property is temperature independent and is shown by all types of substances. Since diamagnetism is much weaker than paramagnetism (1 to 100 times weaker) and both act opposite to each other, it is difficult for the substances having unpaired electrons to show diamagnetism, *i.e.*, the substances having unpaired electrons shows a net paramagnetism.

Q.5. What is ferromagnetism?

Ans.

Ferromagnetism

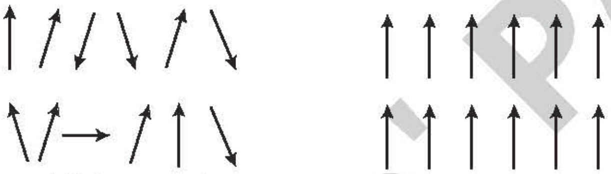
In a normal paramagnetic material, the atoms containing the unpaired electrons are magnetically dilute, and so the unpaired electrons in one atom are not aligned with those in other atoms. However, in ferromagnetic materials, such as metallic iron, or iron oxides such as magnetite (Fe_3O_4), where the paramagnetic iron atoms are very close together, they can create an internal magnetic field strong enough that all the centers remain aligned (Fig. 15).

Q.6. What is antiferromagnetism?

Ans.

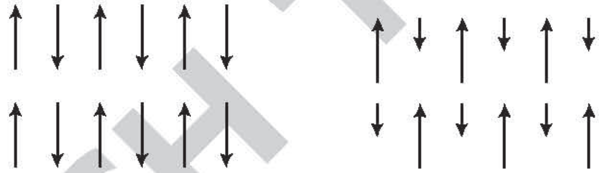
Antiferromagnetism

The spins on the unpaired electrons become aligned in opposite directions so that the μ_{eff} approaches zero, in contrast to ferromagnetism, where μ_{eff} becomes very large. An example of anti-ferromagnetism is found in MnO (Fig. 2).



(a) Paramagnet disordered spins(2D)

(c) ferromagnet ordered (aligned spins (2D)



(b) antiferromagnet

(d) ferrimagnet

Fig. 2 : Types of magnetic behaviour in a substance

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. Describe the selection rule for *d-d* transition.

Ans.

Selection Rule for *d-d* Transition

To define the allowed or forbidden nature of electronic transitions, 2 different selection rules can be used which are given below :

1. **Spin selection rule :** According to the spin selection rule, all the electronic transitions in the transition metal complexes which does not involve the change in the spin multiplicity are called as spin allowed transitions while on the other hand all the electronic transitions which can involve the change in the spin multiplicity are known as spin forbidden transitions, therefore,

$$\Delta S = 0 \text{ (Allowed tranisition)}$$

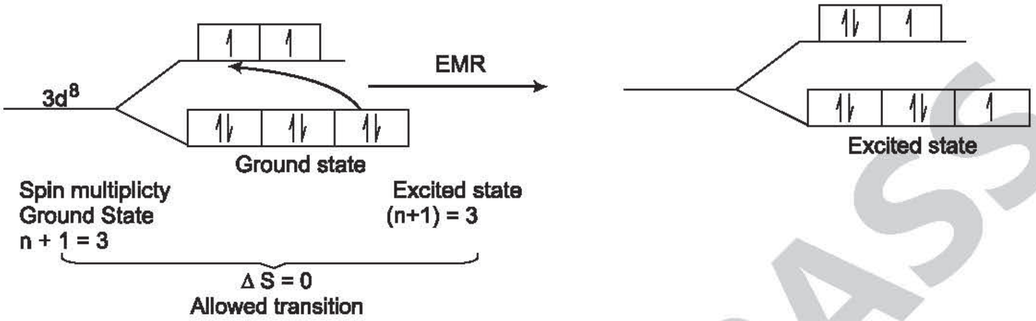
$$\Delta S \# 0 \text{ (Forbidden transition)}$$

Example : (i) **$[Ni(H_2O)_6]^{+2}$ ion :**

$$Ni - 3d^8, 4s^2$$

$$\text{Ni}^{+2} - 3d^8, 4s^0$$

According to CFT :

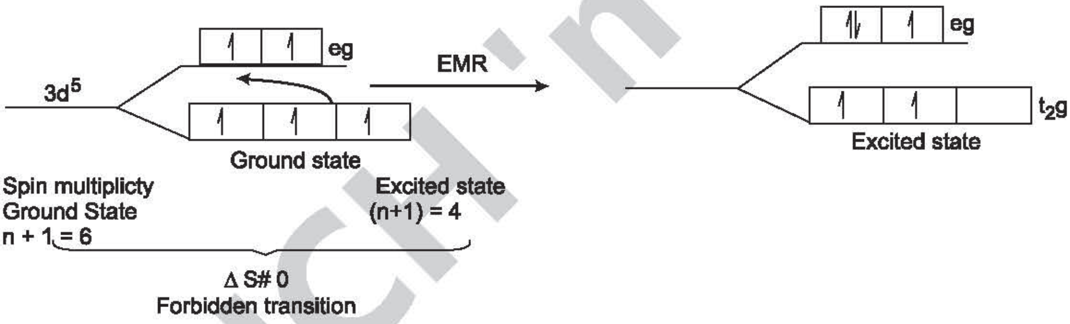


(ii) $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$ **ion :**

$$\text{Mn} - 3d^5, 4s^2$$

$$\text{Mn}^{+2} - 4s^5, 4s^0$$

According to CFT :



2. Laporte selection rule : According to the this rule, all the electronic tranisitions which occur from G(g) to U(u) (gerade to ungerade) or u to g orbitals, are known as Laporte allowed or symmetry allowed transitions while all the electronic tranisitions, which occur from g to g or u to u orbitals are known as Laporte forbidden transition or symmetry forbidden transition.

$$\left.\begin{array}{l} G \longrightarrow U \\ U \longrightarrow G \end{array}\right\}\text{Allowed} \qquad \left.\begin{array}{l} G \longrightarrow G \\ U \longrightarrow U \end{array}\right\}\text{Forbidden}$$

According to this selection rule all the *d-d* transition phenomena in the transition metal complexes bung forbidden.

Therefore, according to the Laporte selection rule, all the electronic transitions in which there does not occur any change in the orbital quantum no (1) value are known as Laporte forbiden transition while all the electronic transitions which involve certain change in the orbital quantum number are known as Laporte allowed tranisiton.

$$\Delta l = 0 \text{ (Laporte forbidden transitions)}$$

$$\Delta l \# 0 \text{ (Laporte allowed transitions)}$$

Thus, according to this selection rule, it is observed that all the *d-d* transitions (*g-g* transitions) are Laporte forbidden. There are certain relaxations in Laporte selection rule due to the possibility of certain extent of *d-p* mixing.

Q.2. Discuss in brief the term symbol and spectroscopic ground state term.

Ans.

Term Symbol and Spectroscopic Ground State Term

In quantum mechanics, the term symbol is the energy level of a single or multi-electron atom which is deduced from total angular momentum quantum number including orbital quantum number and spin quantum number. The atomic term symbols can be calculated from L-S coupling (Russell-Saunders coupling or Spin-Orbital coupling) and the ground state term symbol is predicted by Hund's rules.

Russell-Saunder coupling (Spin orbital or L-S coupling) :

Russell and Saunder have proposed a coupling scheme *i.e.,* Russell-Saunder coupling to calculate the term symbol for the various electronic configurations, which involve the following qaauntum numbers :

1. **Total orbital momentum quantum number or L term :** Vector summation of the 1 values of the different electrons present in a particular configuration is known as total orbital angular momentum quantum number (L term) for the configuration.

   Different symbols for the different L value can be written as :

L	=	0	1	2	3	4	5	6	7
Symbol	=	S	P	D	F	G	H	I	J

2. **Total spin momentum quantum number or S term :** Vector summation of spin angular momentum quantum number of all electrons present in any configuration (s values) is known as total spin angular momentum quantum number or S term.

$$S = \frac{n}{2}$$

   Where, n is the number of unpaired electrons.

3. **Total angular quantum number or J term :** Vector summation of L and S terms for a particular electronic configuration is known as total angular quantum number or J term which arises due to L-S coupling. The values of J are

$$J = L - S, L - S - 1, L - S - 2 \text{ ... upto } L + S$$

   For less than half filled configuration

$$J = L - S$$

   For a configuration which is more than half filled

$$J = L + S$$

4. **Spin multiplicity or M term :** Total number of the possible spin orientations of the unpaired electrons in a particular configuration is known as spin multiplicity or M term.

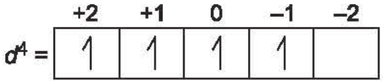
$$\begin{aligned} M &= n + 1 \\ &= 2S + 1 \end{aligned}$$

   Where n = number of unpaired electrons.

According to the above four different terms, term symbol for a particular configuration can be written as

$$^{M}L_{J}$$

For example for d^4 configuration



$$L = 2(D)$$

$$S = \frac{n}{2} = \frac{n}{2} = 2$$

For an electronic configuration less than half filled

$$J = L - S = 0$$

$$M = 4 + 1 = 5$$

So, the term symbol for d^4 configuration is $^{M}L_{J} = {}^{5}D_{0}$.

Term symbol for the various d^n configuration, P^n configuration, S^n configuration can also easily determined.

Hund's rule for ground state term : The calculation of term symbol for the ground state of an atom is relatively easy to using Hund's rules. Ground state term symbol corresponds to a state with maximum S and L values. Each electronic configuration except fully filled has large number of possible arrangements which are known as microstates which can be calculated as follow :

$$\text{Number of microstates} = \frac{n!}{r!(n-r)!}$$

Where n is maximum capacity (maximum number of electrons that can be accommodated in the orbital) of the particular configuration and r is number of electron in the configuration.

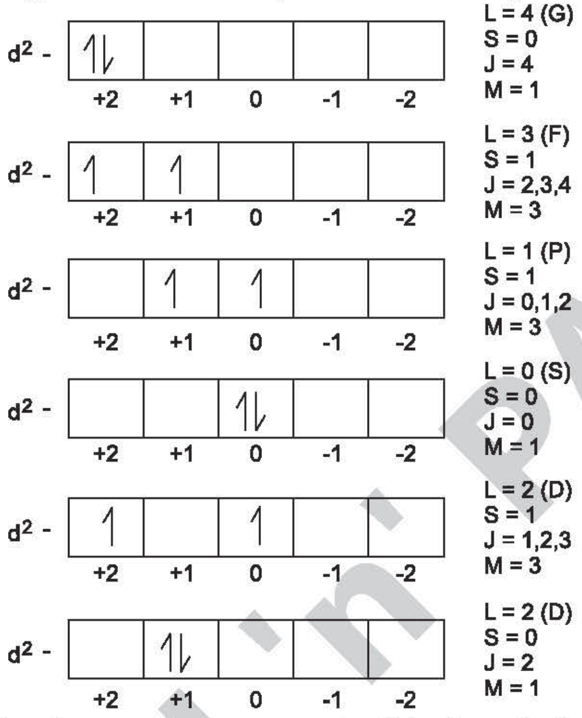
Out of the various possible electronic arrangements, one of the arrangement *i.e.,* ground state electronic arrangement can be calculated with the help of different rule proposed by the Hund, which are given below :

Rule 1 : According to the Hund's rule, out of the various electronic arrangements, the arrangement having the maximum value of spin multiplicity will be the ground state electronic arrangement.

Rule 2 : If more than one electronic arrangement have the same value of spin multiplicity, than the electronic arrangement with higher L value will be the ground state electronic arrangement.

Rule 3 : Among various the ground state electronic arrangements with different J values, if the electronic configuration is less than half filled, than the ground state term will be withleast J value while if the configuration is more than half filled, than the ground state term will be the term with maximum J value.

Example : Evaluation of ground state term symbol for d^2 configuration.



According to the Hund's rule, second arrangement will be the actual ground state electronic arrangement for d^2 configuration. Thus, the term symbol for d^2 configuration will be $^3F_2$.

Q.3. (i) Describe the types of electronic transitions.

(ii) Discuss the electronic spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion.

Ans.

Types of the Electronic Tranisition

Transition metal complexes can exhibit two types of the electronic transitions

1. *d-d* transition
2. Charge transfer transition

1. ***d-d* transition :** In a *d-d* transition, an electron in a *d*-orbital on the metal is excited to another d orbital of higher energy by a photon. In complexes of the transition metals, the *d* orbitals do not all have the same energy. In centrosymmetric complexes, *d-d* transitions are forbidden by the Laporte rule. According to Laporte rule states that, if a molecule is centrosymmetric, transitions within a given set of *p* or *d* orbitals will be forbidden. However, forbidden transitions become allowed if the center of symmetry is disrupted. Transitions that occur as a result of an asymmetrical vibration of a molecule are called vibronic transitions. Through such asymmetric vibrations, transitions that should be theoretically forbidden, such as a *d-d* transition, are weakly allowed.

   d-d-Transition is the phenomena of excitation of the electrons of the splitted lower energy set of *d*-orbitals into the higher energy splitted set of *d*-orbitals by the absorption of electromagnetic radiation is known as phenomena.

Example : In the d^1 configuration containing octahedral complex *i.e.*, $[Ti(H_2O)_6]^{+3}$ ion, the *d-d* transition phenomena is represented in Fig. 3.

$[Ti(H_2O)_6]^{+3}$ ion : Ti $= 3d^2, 4s^2$

Oxidation state of Ti $= +3$

$Ti^{+3} = 3d^1$

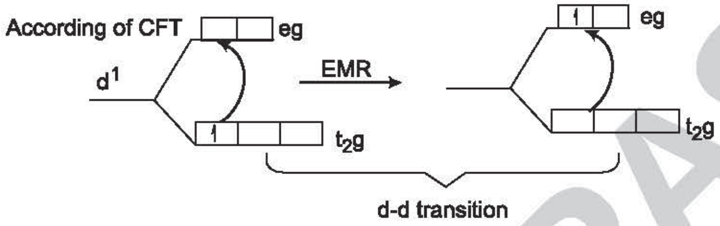


Fig. 3 : *d-d* Tranisition in $[Ti(H_2O)_6]^{+3}$

2. **Charge transfer transition :** In inorganic compounds, most of the charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal like nature and those that are predominantly ligand like nature. If the transfer occurs from the MO with ligand character to the MO with metal-like charcater, the complex is called a ligand-to-metal charge-transfer (LMCT) complex and the transfer is LMCT. If the electronic charge shifts from the MO with metal character to the MO with ligand character, the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, oxidation of the metal center occurs as a result of MLCT, whereas a LMCT results in the reduction of the metal center.

   Depending on the direction of charge transfer, these are classified as either ligand-to metal (LM) or metal-to-ligand (ML) charge transfer :

   (a) **Ligand-to-metal charge transfer (LMCT) :** LMCT complexes arise from the transfer of electrons from MO having ligand character to those having metal character. This type of transfer occurs when complexes have ligands with relatively high-energy lone pairs and if the metal has low-lying empty orbitals. In such complexes, metals have higher uncommon oxidation states or less number of *d*-electrons (even d^0). These conditions suggest that the acceptor metal level is available which is of low energy.

   Consider a d^6 octahedral complex, such as $IrBr_6^{3-}$, whose t_{2g}, orbitals are filled. As a result, an intense absorption peak is observed around 250 nm corresponding to a transition from ligand like σMO to the empty e_g MO of metal like character. However, in case of $IrBr_6^{2-}$, a d^5 complex, two absorption peaks, one near 600 nm and another near 270 nm, are observed. This is because two transitions are possible, one to t_{2g} (that can now accommodate one more electron) and another to e_g. The 600 nm band corresponds to transition of electron from ligand orbital to the t_{2g} MO of metal and the 270 nm band correspond to transfer of electron from ligand MO to the e_g MO of the metal.

Charge transfer bands may also arise from transfer of electrons from nonbonding orbitals of the ligand to the e_g MO of metal.

Examples :

MnO$_4^-$: The permanganate ion with tetrahedral geometry is intensely purple coloured due to strong absorption involving charge transfer from MO of filled oxygen *p*-orbitals to empty MO of manganese (VII).

CdS : The yellow color of cadmium sulphide is due to the transition of electrons from Cd^{2+} $(5s) \leftarrow S^{2-}(\pi)$.

HgS : It is red due to Hg^{2+} $(6s) \leftarrow \mathrm{S}^{2-}(\pi)$ electronic transition.

(b) **Metal-to-ligand charge transfer :** Metal-to-ligand charge-transfer (MLCT) complexes arise as a result of transfer of electrons from MO with metal-like character to those with ligand-like character. These transitions are most common in complexes with ligands having low-lying π orbitals, especially aromatic ligands. For these trasitions to occur, metal should have low oxidation state with sufficient number of electrons and should be relatively high in energy.

Examples :

(i) **Tris (2,2-bipyridyl)ruthenium(II) :** This is a orange-colour complex due to MLCT.

(ii) $\mathrm{W(CO)_4(phen)}$

(iii) $\mathrm{Fe(CO)_3(bipy)}$

(ii) The Electronic Spectrum of $[\mathrm{Ti(H_2O)_6}]^{+3}$ Complex Ion

In $[\mathrm{Ti(H_2O)_6}]^{+3}$ complex, Ti (III) has d^1 configuration and in an octahedral field, the configuration is t_{2g}^1. The t_{2g} level is triply degenerated due to the presence of single electron in the excited state (configuration being e_g^1), Jahn Teller distortion was observed in the absorption spectra of $[\mathrm{Ti(H_2O)_6}]^{+3}$ ion (Fig. 9). Due to tetragonal distortion, the ion was compressed along the *z*-axis. The CFSE will be $2/3\delta_2$ larger than it would have been in a regular octahedron. The excited state (t_{2g}^0 e_g^1 splits due to Jahn Teller distortion. Therefore, the spectrum of the complex ion shows a shoulder as a result of this splitting (Fig. 4) and seems to be comprised of two peaks: one from the ground state to the lower e_g level and the other to the upper e_g level (Fig. 5).

$[\mathrm{Ti(H_2O)_6}]^{+3}$ ion : $\mathrm{Ti} = 3d^2, 4s^2$

Oxidation state of Ti = +3

$\mathrm{Ti}^{+3} = 3d^1$

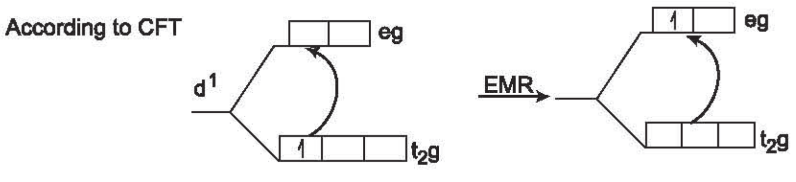


Fig. 4 : ***d-d*** **transition in $[\mathrm{Ti(H_2O)_6}]^{+3}$**

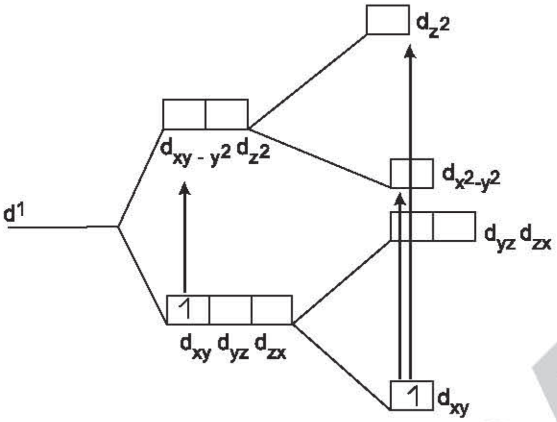


Fig. 5 : Transition in d^1 configuration due to Jahn Teller distortion

Q.4. What is magnetic susceptibility? Describe the various methods of determining magnetic susceptibility.

Ans.

Magnetic Susceptibility

Magnetic susceptibility is a dimensionless proportionality constant that indicates the degree of magnetization of a material in response to an applied magnetic field. It is caused by interactions of electrons and nuclei with the externally applied magnetic field.

In electromagnetism, magnetic susceptibility is defined as :

The measures of how much a material will be magnetized in an applied magnetic field.

It is denoted by χ.

Magnetic Susceptibility Formula : The mathematical definition of magnetic susceptibility is the ratio of magnetization to applied magnetizing field intensity. This is a dimensionless quantity.

$$X = M / H$$

Where, $\chi \rightarrow$ magnetic susceptibility, $M \rightarrow$ magnetization, $H \rightarrow$ field intensity.

Methods of Determining Magnetic Susceptibility

Measurements of magnetic properties have been used to characterize a wide range of systems such as oxides, metallic alloys, solid state materials, and coordination complexes containing metals. Most of the organic and main group element compounds have all the electrons paired and these are diamagnetic molecules with very small magnetic moments. All of the transition metals have at least one oxidation state with an incomplete d sub shell. Magnetic measurements, particularly for the first row transition elements, give information about the number of unpaired electrons. The number of unpaired electrons provides information about oxidation state and electron configuration. The determination of the magnetic properties of the second and third row transition elements is more complex.

The magnetic moment is calculated from the magnetic susceptibility, since the magnetic moment is not measured directly. There are several ways to express the degree to which a material acquires a magnetic moment in a field. The magnetic susceptibility per unit volume is defined by :

$$K = \frac{I}{H}$$

Where I is the intensity of the magnetization induced in the sample by the external magnetic field, H. The extent of the magnetic induction (I) depends on the sample. The induction may be visualized as an alignment of dipoles and/or by the formation of charge polarization in the sample. H is the strength of the external magnetic field in units of oversteds (Oe). The K is unit less.

Generally, it is more convenient to use mass units, therefore, the mass or gram susceptibility (χ_g) is defined as :

$$\chi_g = \frac{K}{d}$$

Where d is the density of the solid. The molar susceptibility (χ_m) is the mass susceptibility multiplied by the formula weight (F.W.).

$$\chi_m = \chi_g \text{ (F.W. in g mol}^{-1}\text{)}$$

The terms κ, χ_g and χ_m are all measures of the magnetic moment of a substance in a magnetic field. There are various methods to measure magnetic susceptibility which are dicussed in the next section.

Gouy's method : Gouy's balance named after the scientist who devised it generally to be used to measure paramagnetism. In this method, finely powdered substance or solution is taken in a pyrex cylindrical glass tube called Gouy tube the substance is weighed first without magnetic field and then in the presence of magnetic field (Fig. 3.2). A paramagnetic substance will weigh more in the presence of a magnetic field than in its absence, the increase in weight gives a quantification of paramagnetism of the substance. More the number of unpaired electrons in a substance; greater will be the increase in its weight under a magnetic field. The magnetic susceptibility is measured from the difference in weight of the sample with and without magnetism.

Determination of magnetic moment

Measurement with standard substance : The apparatus can be calibrated by measuring the values of a substance whose susceptibility is accurately known. The standard substance commonly used for calibration is mercury tetrathiocynatocobaltate; $Hg[Co(CNS)_4]$. Its magnetic susceptibility is 16.44×10^{-6} at 20°C.

I. Weigh the empty tube with and without magnetic field in gram.

Weight of empty tube without magnetic field = A

Weight of empty tube with magnetic field = B

Difference in weights of empty tube = $B - C$

II. Weigh the tube filled with standard substance in presence and in absence of magnetic field in gram

Weight of tube filled with the standard in absence of magnetic field = D

Weight of tube filled with the standard in presence of magnetic field = E

Difference in weight of tube filled with standard = $E - D$

III. Difference in the weight of standard $(\Delta w_s) = (E - D) - (B - A)$

IV. Weight of standard in absence of magnetic field $(w_s) = D - A$.

Measurement with unknown substance

I. Weigh the empty tube with and without magnetic field in gram

Weight of empty tube without magnetic field = F

Weight of empty tube with magnetic field = G

Difference in weights of empty tube = $G - F$

II. Weigh the tube filled with substance in presence and in absence of magnetic field in gram

Weight of tube filled with substance the in absence of magnetic field = H

Weight of tube filled with the substance in presence of magnetic field = I

Difference in weight of tube filled with substance $= I - H$

III. Difference in the weight of substance $(\Delta w) = (I - H) - (G - F)$

IV. Weight of substance in absence of magnetic field $(w) = H - F$

If magnetic susceptibility of the standard is χ_s then the magnetic susceptibility of the substance will be

$$\chi = \chi_s \frac{W_s}{\Delta W_s} \times \frac{\Delta W}{W}$$

$\chi_m = \chi \times$ molecular weight of the substance

The Gouy method is a convenient method for measuring magnetic susceptibility. The sample is suspended (in a cylinder) in a non homogeneous magnetic field and the force exerted on the sample can be determined by weighing it. The force acting on the sample is

$$F = \frac{1}{2} AH^2 \kappa$$

Where A is the cross sectional area of the cyclinder; H is the intensity in the central homogenous part of the magnetic field and κ is volume susceptibility.

The above equation is valid only when the measurements are taken in vacuum. However, if the sample is surrounded by air, then the air susceptibility (κ') must be subtracted from the measured susceptibility. Now the equation becomes :

$$F = \frac{1}{2} AH^2 (\kappa - \kappa')$$

Where κ' is the volume susceptibility of air.

The Gouy tube itself produces a force which is always present. Therefore, actual force acting on the sample can be calculated by subtracting the force acting on the Gouy tube (δ) from the observed force. This force will be negative because of the diamagnetic material of the tube. Now the equation becomes :

$$F = \frac{1}{2} \Delta H^2 (\kappa - \kappa') + \delta$$

For a sample with constant length and cross sectional area, the factor AH^2 will be constant. If the sample density is introduced, the above equation can be written as :

$$10^6 \chi = \frac{\alpha + \beta F}{w}$$

Where α is a constant for the displaced air = 0.029 × specimen volume and expressed in mg; w is the weight of sample in gram; F is the force on the sample and β = tube calibration constant.

The apparatus can be calibrated by measuring the values of a substance whose susceptibility is accurately known. The standard substance commonly used for calibration is mercury tetrathiocynatocobaltate; $Hg[Co(CNS)_4]$. Its magnetic susceptibility is 16.44×10^{-6} at 20°C. By taking measurements with this standard substance, the constant β is first calculated. By substuting the values of α, β, δ and $F\, F$ on a sample of weight w, the susceptibility (χ) of the substance can be calculated.

The forces are large because the amount of sample taken in the Gouy's tube is quite large and therefore, a chemical balance can also measure the changes in mass. The disadvantage of this method is that it requires perfect uniform packing of the substance in the Gouy's tube. Therefore, correct results can not be obtained if the Gouy's tube has not been packed uniformly.

Quinckes method

The Quincke's method is used to calculate magnetic susceptibility of diamagnetic or paramagnetic substances in a liquid form. When an object is placed in a magnetic field, a magnetic moment is induced in it. Magnetic susceptibility of a magnetic substance is the ratio of the magnetization I (magnetic moment per unit volume) to the applied magnetizing field intensity H. The magnetic moment can be measured either by force methods or induction methods. The Quincke's method like the Gouy's method belongs to force method. The force on the sample is negative of the gradient of the change in energy density when the sample is placed in magnetic field.

$$f = \frac{d}{dx}\left[\frac{1}{2}\mu_0 (\mu_r - \mu_{ra}) H^2\right] = \frac{1}{2}\mu_0 (x - x_a) \frac{d}{dx} H^2 \qquad ...(1)$$

Here, μ_0 is permeability of the free space and μ_r, χ and μ_{ra}, χ_a are relative permeability and susceptibility of the sample and the air respectively which the sample displaces. The force acting on an element of area A and length dx of the liquid column is $fAdx$. Therefore, the total force F on the liquid is

$$F = A\int f dx = \frac{A\mu_0}{2}(\chi - \chi_a)(H^2 - H_0^2) \qquad ...(2)$$

H is equal to the field at the liquid surface between the poles of the magnet and 0. The liquid of density r moves under the influence of this force until it is balanced by the pressure exerted over the area A due to a height difference of h between the liquid surfaces in the two arms of the U-tube. Therefore, the force will be

$$F = Ah(\int - \int a)g$$

Or

$$\chi = \chi_a + \frac{2}{\mu_0} g(\int - \int a) \frac{h}{(H^2 - H_0^2)} \qquad ...(3)$$

In actual practice χ_a, density of air ρ_a and H_0 are negligible and can be ignored and the above expression simplifies to

$$\chi = 2\int \frac{gh}{\mu_0 H^2} \qquad ...(4)$$

This equation shows that by plotting h as a function of H^2, the susceptibility χ (called the volume susceptibility) can be determined directly from the slope of the straight line graph. It is a dimensionless quantity. This expression is in S.I. units in which ρ, g, h and H are measured in kg/m^3, m/s^2, m and amp. turn/m respectively.

In C.G.S. units, equation (3) and (4) are

$$\chi = \chi_a + 2g(\rho - \rho_a)\frac{h}{(H^2 - H_0^2)} \qquad ...(5)$$

$$\chi = \frac{2\rho g h}{H^2} \qquad ...(6)$$

Where ρ, g, h and H are measured in g/cm^3, cm/s^2, cm and gauss respectively. The volume susceptibilities in the two systems of units are related as χ (SI units) $= 4\chi$ (CGS units).

Q.5. (i) Write a note on spin only formula.

(ii) Discuss in brief spin and orbital contribution to magnetic moments.

Ans.

(i) Spin Only Formula

We begin the discussion of magnetochemistry with the so called spin-only formula, an approximation that has limited, but useful, applications. Paramagnetism arises from unpaired electrons. Each electron has a magnetic moment with one component associated with the spin angular momentum of the electron and (except when the quantum number $1 = 0$) a second component associated with the orbital angular momentum. For many complexes of first row *d*-block metal ions we can ignore the second component and the magnetic moment, μ can be regarded as being determined by the number of unpaired electrons, n (equation 1 & 2). The two equations are related because the total spin quantum number $S = \frac{n}{2}$.

$$\mu \text{ (spin only)} = 2\sqrt{S(s+1)} \qquad ...(1)$$

$$\mu \text{ (spin only)} = \sqrt{n(n+2)} \qquad ...(2)$$

The effective magnetic moment, μ_{eff}, can be obtained from the experimentally measured molar magnetic susceptibility, χ_m and is expressed in Bohr magnetons (BM) where 1 BM $= 9.27 \times 10^{-24}$ Joule T^{-1}. Equation (3) gives the relationship between μ_{eff} and χ_m; using SI units for the constants, this expression reduces to equation (4) in which χ_m is in cm^{3}mol^{-1}.

$$\mu_{eff} = \sqrt{\frac{3k\chi_m T}{L\mu_0 \mu B^2}} \qquad ...(3)$$

where k = Boltzmann constant; L = Avogadro number; μ_0 = vacuum permeability; T = temperature in Kelvin and χ_m is the molar suscptibility.

$$\mu_{eff} = 0.7977\sqrt{\chi_m T} \qquad ...(4)$$

Spin-only values of μ_{eff} compared with approximate ranges of observed magnetic moments for high-spin complexes of first row d-block ions can be seen by following table

Table : Comparison between the spin only and observed magnetic moments in high spin complexes of first row transition elements

Metal ion	d^n configuration	S	μ_{eff} (spin only) BM	Observed values of μ_{eff} BM
Sc^{+3}, Ti^{+4}	d^0	0	0	0
Ti^{+3}	d^1	1/2	1.73	1.7-1.8

V^{+3}	d^2	1	2.83	28.-3.1
V^{+2}, Cr^{+3}	d^3	3/2	2.87	3.7-3.9
Cr^{+2}, Mn^{+3}	d^4	2	4.90	4.8-4.9
Mn^{+2}, Fe^{+3}	d^5	5/2	5.92	5.7-6.0
Fe^{+2}, Co^{+3}	d^6	2	4.90	5.0-5.6
Co^{+2}	d^7	3/2	3.87	4.3-5.2
Ni^{+2}	d^8	1	2.83	2.9-3.9
Cu^{+2}	d^9	1/2	1.73	1.9-2.1
Zn^{+2}	d^{10}	0	0	0

(ii) Spin and Orbital Contribution to Magnetic Moments

Various complexes of transition metals (mostly first transition series elements) give a magnetic moment much higher than μ_S. This is due to the orbital contributions to magnetic moment. The spin angular momentum of an electron is independent of its surroundings and therefore, the spin moment of unpaired electron remains, unaffected by changes in chemical bonding of the compound provided that there is no spin pairing because of bonding. On the conflicting, the orbital angular momentum of the electron depends upon the chemical environment. The orbital contribution of magnetic moment may get compensated or quenched.

Thus, as a result, the observed magnetic moments are very close to spin only magnetic moment value.

The quenching of orbital angular momentum can be easily explained on the basis of Crystal Field Theory of bonding in transition metal complexes.

The unpaired electrons in a first transition series are present in the 3*d* orbitals. A transition metal ion has five 3*d* orbitals which are degenerate. An electron possesses as angular momentum along a given axis if it is possible to transform its orbital by rotation around this axis into another orbital which is equivalent to it in shape, axis and energy.

Thus, for orbital contribution to the magnetic moment, there must be two or more degenerate orbitals which can be inter converted by rotation about a suitable axis and these orbitals must be unequally occupied.

The orbital angular momentum along the given axis possessed by the electron in such an orbital is equal to the number of times the orbital gets transformed in to the equivalent orbital during a rotation of 90° around that axis. If the orbital degeneracy is lost by chemical bonding or crystal field effects, the orbital contribution to the total magnetic moment is partially or completely quenched.

Let us consider a free metal ion in which all the *d*-orbitals are degenerate. An electron in $d_{x^2-y^2}$ orbital will contribute to orbital angular momentum equal to 2 units of $h/2\pi$ along *z*-axis because a rotation of $d_{x^2-y^2}$ orbital by 45° around the *z*-axis takes it to equivalent d_{xy} orbital (Fig. 6).

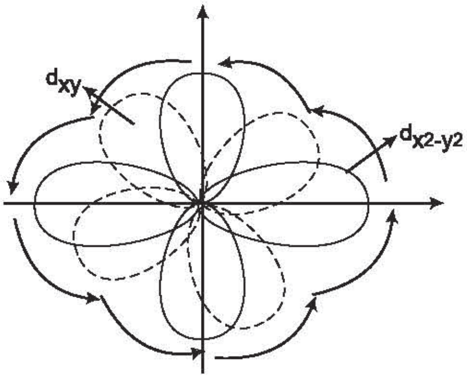


Fig. 6 : Circulation of electron density about *z*-axis in d_{xy} and $d_{x^2-y^2}$ orbitals

In the above discussion, it is clear that a rotation of $d_{x^2-y^2}$ orbital by 90° around z-axis will carry this orbital in to d_{xy} orbital 2 times. Similarly, we can also say that an electron in d_{xy} orbital will contribute to orbital angular momentum of two in the units of $h/2\pi$ along z-axis. Similarly, an electron in d_{xz} orbital will have an orbital angular momentum equal to 1 unit of $h/2\pi$ along z-axis because d_{xz} orbital gets transformed into an equivalent d_{yz} orbital by rotating the d_{xz} orbital around x-axis by an angle of 90°.

When the metal ion is surrounded octahedrally by six ligands, the degeneracy of d-obritals gets disturbed. The d_{xy} and $d_{x^2-y^2}$ orbitlas acquire different energies and therefore, are non-equivalent. As a result, an electron in $d_{x^2-y^2}$ orbtial cannot be equated with an electron in d_{xy} orbital. In other words, the $d_{x^2-y^2}$ orbital cannot be transformed into d_{xy} orbital and vice versa by rotation of the orbital along z-axis. Thus, the electron in $d_{x^2-y^2}$ orbital will not cause to have orbital contribution along the z-axis.

Q.6. Describe in detail L-S coupling.

Ans.

L-S Coupling

Russell-Saunders coupling, also known as **LS coupling**, specifies a coupling scheme of electronic spin- and orbital-angular momenta. The coupling scheme is named after H.N. Russell and F. A. Saunders (1925). Russell-Saunders coupling is useful mainly for the lighter atoms, roughly for atoms with atomic number less than 57. For heavier atoms j-j coupling gives a better approximation for atomic wave function.

Description

Consider an atom with n electrons. In Russell-Saunders coupling the orbital angular momentum eigenstates of these electrons are coupled to eigenstates with quantum number L of the total angular momentum operator squared L^2, where the angular momentum operator is

$$L = \sum_{i=1}^{n} 1 \qquad \text{...(1)}$$

Separately the one-electron spin functions are coupled to eigenstates with quantum number S of total spin angular momentum squared S^2. Sometimes there is further coupling to $\boldsymbol{J} \equiv \boldsymbol{L} + \boldsymbol{S}$. The resulting L-S eigenstates are characterized by term symbols.

Consider, as an example, the excited helium atom in the atomic electron configuration $2p3p$. By the triangular conditions the one-electron spins $s = 1/2$ can couple to $|1/2 - 1/2|, 1/2 + 1/2 = 0, 1$ (spin singlet and triplet) and the two orbital angular momenta $l = 1$ can couple to $L = |1 - 1|, 1, 1 + 1 = 0, 1, 2$. In total, Russell-Saunders coupling gives two-electron states labeled by the term symbols

$$^1S, \; ^1P, \; ^1D, \; ^3S, \; ^3P, \; ^3D.$$

The dimension is $1 \times (1 + 3 + 5) + 3 \times (1 + 3 + 5) = 36$. The electronic configuration $2p3p$ stands for $6 \times 6 = 36$ orbital products, as each of the three p-orbitals has two spin functions, so that in total there are 6 spinorbitals with principal quantum number $n = 2$ and also 6 spinorbitals with $n = 3$. A check on dimensions before and after coupling is useful because it is easy to overlook coupled states.

Russell-Saunders coupling gives useful first-order states in the case that one-electron spin-orbit coupling is much less important than the Coulomb interactions between the electrons and can be neglected. This occurs for the low Z part (*i.e.*, the lighter elements) of the periodic table, roughly up to the lanthanoids (previously lanthanides, starting at $Z = 57$). The usefulness stems from the fact that states of different L and S do not mix under the total Coulomb interaction, so that LS coupling achieves a considerable block diagonalization of the matrix of a Hamiltonian in which spin-orbit coupling is absent.

In the high Z regions of the periodic system it is common to first couple the one-electron momenta $j \equiv l + s$ and then the one-electron j-eigenstates to total J. This so-called j-j coupling scheme gives a more useful first-order approximation when spin-orbit interaction is larger than the Coulomb interaction and spin-orbit interaction is included, while the Coulomb interaction is neglected. If, however, in either coupling scheme all resulting states are accounted for, i.e., the same subspace of Hilbert (function) space is obtained, then the choice of coupling scheme is irrelevant in calculations where both interactions-electrostatic and spin-orbit-are included on equal footing.

More complicated electron configurations

Spin coupling : Let us consider how to couple n spin-1/2 particles (electrons) to eigenstates of total S^2.

The one-electron system ($n = 1$) has two functions with $s = 1/2$ and $m = +1/2$ (spin up and down). It was shown that addition of an electron leads to four two-electron spin functions : a singlet ($2S + 1 = 1$) and a triplet space (a "ladder" of $2S + 1 = 3$ spin functions). If one adds one spin to the two-electron triplet ($S = 1$), the triangular conditions tell us that $S = 3/2$, and $S = 1/2$ can be obtained. In the diagram on the right we see that two lines depart from the $n = 2, S = 1$ node. One line goes up and joins the $n = 3, S = 3/2$ node, the other goes down and joins the $n = 3, S = 1/2$ node.

A two-particle spin system also has a spin-singlet $S = 0$. Adding a spin to it leads to a doublet, $S = 1/2$. It can be shown that the doublet thus obtained is orthogonal to the doublet with the intermediate ($n = 2, S = 1$) spin triplet.

Two different paths lead two different : even orthogonal : three-electron spin doublets. This is why the number 2 is listed in the circle at the $n = 3, S = 1/2$ node.

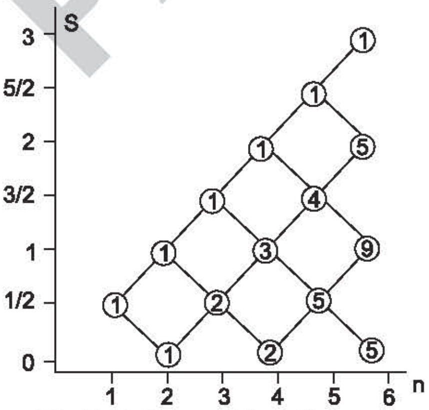


Fig. 7 : Spin branching diagram. Number of electrons n on the abscissa. Spin quantum number S on the ordinate

From the two doublets it is possible, by again adding one electron, to create two four-electron singlets, and two four-electron triplet spaces (ladders). A four-electron triplet space can also be obtained from the three-electron quadruplet ($S = 3/2$) by subtracting $S = 1/2$. Hence the number 3 is found at the $n = 4, S = 1$ node. It is the sum of numbers in the nodes directly on its left connected to it.

The system of sequentially coupling one electron at the time should be clear now. Every path in the branching diagram corresponds to a unique $(2S+1)$-dimensional ladder of eigenfunctions of total spin angular momentum operator S^2 with spin quantum number S. Ladders belonging to different paths are orthogonal. The number in the circle indicates how many paths have this node as endpoint.

It is of interest to check dimensions. For instance, the total spin space of five electrons is of dimension $2^5 = 32$. Reading from bottom to top in the diagram, one finds $5 \times 2 + 4 \times 4 + 1 \times 6$ (second factors being $2S + 1$), which indeed adds up to 32.

The actual coupling of electron n to a state of $n-1$ electrons uses special values of Clebsch-Gordan coefficients. Let us use k as a path index (*e.g.,* for $S=1$ and $n=6$, the index k runs from 1 to 9). Then addition (line upwards) gives the n-electron spin state :

$$|k,S,M\rangle=\sqrt{\frac{1}{2S}}\left(\sqrt{S+M}\left|k,S-\frac{1}{2},M-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle+\sqrt{S-M}\left|k,S-\frac{1}{2},M+\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right)$$

Subtraction (line downwards) gives the n-electron spin state :

$$|k,S,M\rangle=\sqrt{\frac{1}{2S+2}}\left(-\sqrt{S-M+1}\left|k,S+\frac{1}{2},M-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle+\sqrt{S+M+1}\left|k,S+\frac{1}{2},M+\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right)$$

In particular, for $n=2$ the spin triplet results :

$$|1,1,M\rangle=\sqrt{\frac{1}{2}}\left(\sqrt{1+M}\left|1,\frac{1}{2},M-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle+\sqrt{1-M}\left|1,\frac{1}{2},M+\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right)$$

which gives the triplet "ladder", where in the notation the index $k=1$ is suppressed,

$$|1,1\rangle=\left|\frac{1}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle\equiv\alpha\,(1)\,\alpha\,(2)$$

$$|1,0\rangle=\sqrt{\frac{1}{2}}\left(\left|\frac{1}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle+\left|\frac{1}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right)\equiv\sqrt{\frac{1}{2}}\,(\beta(1)\,\alpha(2)+\alpha(1)\,\beta(2))$$

$$|1,-1\rangle=\left|1,\frac{1}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\equiv\beta(1)\,\beta(2)$$

Here the more common notation for one-electron spin functions (α for m = 1/2 and β for m = −1/2) is introduced. Note that all three triplet spin functions are symmetric under interchange of the two electrons.

The two-electron spin singlet follows from (suppressing the path index $k=1$ again) :

$$|0,0\rangle=\sqrt{\frac{1}{2}}\left(-\left|\frac{1}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle+\left|\frac{1}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right)\equiv\sqrt{\frac{1}{2}}\,(\alpha(1)\,\beta(2)-\beta(1)\,\alpha(2))$$

a function that is antisymmetric (changes sign) under permutation of electron 1 and 2.

Orbital coupling

The one-electron orbital angular momenta l can also be coupled sequentially, *i.e.,* one after the other. Different paths give orthogonal states. Consider as an example the configuration p^3. Repeated application of the triangular conditions gives that $3^3=27$ dimensional space decomposes as follows in eigenspaces of L^2, [with $L\equiv l\,(1)+l(2)+l(3)$] :

$$(2)F,(2)D,(1)D,(2)P,(1)P,(0)P,(1)S$$

where the two-electron quantum numbers L_{12} of electron 1 and 2 precede in brackets the letters designating the three-electron angular momentum quantum number, Dimensions are: 7 + 5 + 5 + 3 + 3 + 3 + 1 = 27. There are two orthogonal D spaces and three orthogonal P spaces, while there is only one F and S space (of dimension 7 and 1, respectively).

The algorithm should be clear now. For instance, to decompose the 135-dimensional space belonging to the configuration p^3d, one can use the result for p^3 and add d to any of the eigenspaces and use the triangular conditions again, as in $F\times d$ gives $L=5,4,3,2,1$.

Equivalent electrons

So far it was ignored the Pauli principle that states that many-electron wave functions must be antisymmetric under simultaneous transposition of spatial and spin coordinates of any pair of electrons. This principle affects considerably the results for configurations of **equivalent** electrons, which by definition are electrons with the same *n* (principal) and *l* (azimuthal or angular momentum) quantum numbers. It will be shown that certain terms (*LS* states) arising from equivalent electrons are forbidden by the Pauli principle. Terms arising from non-equivalent electrons are never forbidden, they simply give rise to non-vanishing antisymmetric states.

Two-electron atoms

Let us take as an example the spatial product, describing two equivalent electrons, $2p_x(1)\,2p_x(2)$. Transposition $P_{(12)}$ of space coordinates gives in general :

$$P_{(12)}\,,\, p_i(1)\,p_j(2) = p_i(2)\,p_j(1) \equiv p_j(1)\,p_i(2).$$

Hence, $$P_{(12)}\,p_x(1)\,p_x(2) = p_x(1)\,p_x(2),$$

and it follows that the product is symmetric under transposition.

So, there are two-electron singlet and triplet spin functions. In both cases $M_S = 0$ functions are considered, thus,

$$|p_x^2, S=0, M_S=0\rangle \equiv 2p_x(1)\,2p_x(2)\,(\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2))/\sqrt{2}$$

$$|p_x^2, S=1, M_S=0\rangle \equiv 2p_x(1)\,2p_x(2)\,(\alpha(1)\beta(2) + \beta(1)\,\alpha(2))/\sqrt{2}$$

Antisymmetric functions, satisfying the Pauli principle, are obtained by use of the antisymmetrizer $A = [(1) - (12)]/2$, where (12) transposes simultaneous space and spin coordinates of electron 1 and 2 and (1) is the identity operator (does nothing)

$$\begin{aligned} 2A\,|p_x^2, S=0, M_S=0\rangle &= 2p_x(1)\,2p_x(2)\,(\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2))/\sqrt{2} \\ &\quad - 2p_x(2)\,2p_x(1)\,(\alpha(2)\,\beta(1) - \beta(2)\,\alpha(1))/\sqrt{2} \\ &= 2\,[2p_x(1)\,2p_x(2)\,(\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2))/\sqrt{2}] \end{aligned}$$

Hence, $$A|p_x^2, S=0, M_S=0\rangle = |p_x^2, S=0, M_S=0\rangle$$

It follows that the symmetric spatial function $2p_x(1)\,2p_x(2)$ multiplied by the antisymmetric spin singlet function is an eigenfunction of the antisymmetrizer, that is, the symmetric space times antisymmetric spin function satisfies the Pauli principle.

The calculation for the spin triplet is repeated :

$$\begin{aligned} 2A|p_x^2, S=1, M_S=0\rangle &= 2p_x(1)\,2p_x(2)\,(\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2))/\sqrt{2} \\ &\quad - 2p_x(2)\,2p_x(1)\,(\alpha(2)\,\beta(1) + \beta(2)\,\alpha(1))/\sqrt{2} \\ &= 0 \end{aligned}$$

Hence, $$A|p_x^2, S=1, M_S=0\rangle = 0$$

The symmetric spatial function $2p_x(1)\,2p_x(2)$ multiplied by the symmetric spin triplet function does not have a non vanishing antisymmetric component, that is, this space-spin product is forbidden by the Pauli principle.

So, this example shows clearly two important results valid for two particles :

1. Spin eigenfunctions of S^2 are either symmetric or antisymmetric under transposition of spin coordinates.
2. The symmetric orbital function multiplied by a symmetric spin function is Pauli forbidden, *i.e.*, vanishes upon antisymmetrization. The same function multiplied by an antisymmetric spin function is antisymmetric under simultaneous transpositions of space and spin coordinates, and hence is Pauli allowed.

Conversely, it can be shown that an antisymmetric orbital function, for instance : $p_x(1)\,p_y(2) - p_x(2)\,p_y(1)$, can only combine with a symmetric spin function to a non-vanishing-Pauli allowed—totally antisymmetric spin—orbit function.

In general one can show from the symmetry of the Clebsch-Gordan coefficients that eigenstates of L^2 for two equivalent electrons with odd quantum number L are antisymmetric under transposition of the electron coordinates. Hence these odd L states must be multiplied by symmetric spin functions (triplets $S = 1$). In total $L + S$ must be even. The even L states (still for two equivalent electrons) are even under transposition and must be multiplied by odd spin functions (singlets, $S = 0$). Again $L + S$ must be even in order to get a non-vanishing result upon antisymmetrization.

Before continuing, it must be pointed out that there exists an interesting symmetry between **holes** and **particles**. If an electron from a closed subshell is removed a hole is prepared in the subshell. It can be shown that a hole shares many properties with an electron, it has the same orbital and spin angular momentum quantum number. A number of holes must satisfy the Pauli principle in the very same way as an equal number of electrons.

The rule is : $L + S$ must be even for two equivalent electrons. This rule also holds for two equivalent holes. Thus, for instance the carbon atom ground state has two equivalent electrons: $1s^2 2s^2 2p^2$, which gives ${}^3P$, ${}^1D$ and ${}^1S$. The oxygen atom ground state has two equivalent holes : $1s^2 2s^2 2p^4$, which also gives ${}^3P$, ${}^1D$ and ${}^1S$.

Knowing all this one can construct the following table :

$$(ns)^2 \rightarrow {}^1S$$

$$(np)^2, (np)^4 \rightarrow {}^1S, {}^1D, {}^3P$$

$$(nd)^2, (nd)^8 \rightarrow {}^1S, {}^1D, {}^1G, {}^3P, {}^3F$$

$$(nf)^2, (nf)^{12} \rightarrow {}^1S, {}^1D, {}^1G, {}^1I, {}^3P, {}^3F, {}^3H$$

Many-electron atoms : When considering more than two electrons, one can ignore closed (sub) shells in the Russell-Saunders coupling because they have $L = S = 0$.

For more than two electrons (or holes) the theory based on the symmetric group can be extended. It can be shown that an N-electron spin eigenfunction of S^2 belongs to an irreducible representation of the symmetric group (also known as permutation group) S_N. In other words, the concept of symmetry under transpositions can be generalized to more than two particles. This generalized permutation symmetry is enforced on the spin functions by requiring them to be eigenfunctions of S^2, a Casimir operator of the group $SU(2)$. The irreducible representations of $SU(2)$ and S_N carried by tensor space are intertwined. The antisymmetrizer acting on an orbital product times an eigenfunction of S^2 enforces permutational symmetry on the orbital product (carries, so to speak, the permutation symmetry of the spin part over to the orbital part). The permutational symmetry of the orbital product, finally, implies that the orbital product is adapted to the unitary group $U\ (2l+1)$. The irreducible representations of the latter group carry different eigenstates of L^2, that, by construction, are Pauli allowed. This procedure is elegant and not very tedious, but requires some knowledge of group theory, in particular knowledge of the connection between the irreducible representations of $SU(2)$, S_N and $U(2l+1)$ carried by N-fold tensor product spaces. The conventional, much more tedious, non group-theoretical, way to proceed is by a "bookkeeping" procedure. Basically, one tabulates all the combinations of one-electron quantum numbers allowed by the Pauli principle and determines the combination with highest M_L and M_S, which are given by the respective sums of the orbit- and spin-magnetic quantum numbers of the individual electrons. This combination is unique and defines "ladders" of eigenstates with $L = M_L^{\max}$ and $M_S^{\max}$. One removes the ladders starting with these maximum values from the table and searches for the next unique combination of highest M_L and M_S that are left in the table. This is repeated until the table is empty and all ladders (LS states) have been assigned.

It is of some historical interest to remark that the latter procedure was followed by Hund in 1925, before the discovery of spin or introduction of Slater determinants. The following table is a combination of Tables 3 and 4 of Hund (with the correction of two "bookkeeping" errors made by Hund, proving that this procedure is error prone).

Term symbols deriving from configurations of equivalent electrons

Configuration	Terms
p, p^5	^2P
p^2, p^4	$^1S,\ ^1D,\ ^3P$
p^3	$^2P,\ ^2D,\ ^4S$
d, d^9	^2D
d^2, d^8	$^1S,\ ^1D,\ ^1G,\ ^3P,\ ^3F$
d^3, d^7	$^2P,\ ^2D,\ ^2D,\ ^2F,\ ^2G,\ ^2H,\ ^4P,\ ^4F$
d^4, d^6	$^1S,\ ^1S,\ ^1D,\ ^1D,\ ^1F,\ ^1G,\ ^1G,\ ^1I,\ ^3P,\ ^3P,\ ^3D,\ ^3F,\ ^3F,\ ^3G,\ ^3H,\ ^5D$
d^5	$^2S,\ ^2P,\ ^2D,\ ^2D,\ ^2D,\ ^2F,\ ^2F,\ ^2G,\ ^2G,\ ^2H,\ ^2I,\ ^4P,\ ^4D,\ ^4F,\ ^4G,\ ^6S$

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MODEL PAPER

Chemical Dynamics and Coordination Chemistry

B.Sc.-II (SEM-III) [M.M. : 75

Note : Attempt all the sections as per instructions.

Section-A : Very Short Answer Type Questions

Instruction : Attempt all **FIVE** questions. Each question carries **3 Marks**. Very Short Answer is required, not exceeding 75 words. **[3 × 5 = 15]**

1. What is the unit of rate of a reaction?
2. Which properties do remain constant in the following equilibrium?
3. Sort out the cationic, anionic and neutral complexes among the following : $K_2[HgI_4]$, $[Co(NH_3)_6]Cl_3$, $K_3[Fe(CN)_6]$, $[Ni(CO)_4]$, $[Pt(NH_3)_2Cl_2]$, $[Fe(H_2O)_6]Cl_3$.
4. What is the relation between mass and number of moles of a gas?
5. State whether a complex formed by sp^3d^2 hybridisation is a low spin or a high spin complex.

Section-B : Short Answer Type Questions

Instruction : Attempt all **TWO** questions out of the following 3 questions. Each question carries **7.5 Marks**. Short Answer is required not exceeding 200 words. **[7.5 × 2 = 15]**

6. What are the differences between molecularity and order of reaction.
7. What do you mean by phase and degree of freedom?
8. Write a short note on liquids.

Section-C : Long Answer Type Questions

Instruction : Attempt all **THREE** questions out of the following 5 questions. Each question carries **15 Marks**. Answer is required in detail, between 500-800 words. **[15 × 3 = 45]**

9. What do you mean by rate of a chemical reaction? Discuss rate of reaction and rate constant. Also give the units of rate constant.
10. Derive law of mass action thermodynamically.
11. Discuss the causes of deviation from ideal gas behaviour. How they are accounted for in van der Walls equation.
12. Describe the IUPAC momenclature of co-ordination compounds. How to write the formula of a simple mononuclear complex from its IUPAC name? Give some examples.
13. What are orgel energy diagram? Discuss the orgel energy diagrams for d^9, d^1, d^2 and d^8 states.

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