

# Chemistry

## Short Answer Collection

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B.Sc 3rd Semester

Chemical Dynamics and  
Coordination Chemistry

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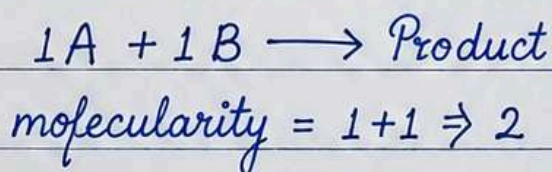


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Q.1 Write the difference between molecularity and order of reaction.

### Molecularity

(i) It is equal to the total no. of reactant molecule in the reaction.



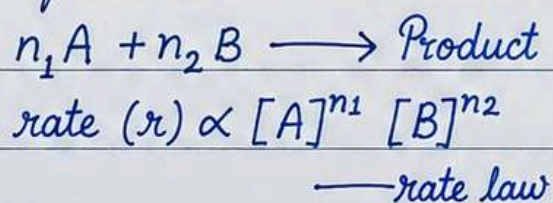
(ii) It is an theoretical value.

(iii) It can not be equal to zero / -ve.

(iv) It is always in natural no. 0, 1, 2, 3.

### Order of reaction

(i) It is the sum of powers of conc. term in rate law equation. As -



$$\text{Order} = (n_1 + n_2)$$

(ii) Order of reaction is an experimental value.

(iii) The order of reaction may be zero.

(iv) It can have also fractional value as  $1, 1/2, 3/2, 5/2, \dots$

Q.2 Deduce an expression for the rate constant of first order reaction.

Integrated rate eqn for first Order rxn :-

In this rxn, the rate depends on the first power (one conc. term) of reactant conc.

A (reactant)  $\longrightarrow$  Product  
at initial amt. 0  
(t=0)

after time t (a-x) mol. x mol.

$\therefore$  for 1<sup>st</sup> order rxn —

$$\text{rate}(x) \propto [A]^1 \quad \text{rate}(x) = -\frac{d[A]}{dt} \propto [A]^1$$

$$dx \propto (a-x)^1$$

$$= -\frac{d[A]}{dt} \propto (a-x)^1$$

$$\frac{dx}{dt} = k_1(a-x)^1 \dots \text{eq(i)}.$$

$$= -\frac{d[A]}{dt} = k_1(a-x)^1$$

$$\frac{dx}{dt} = k_1(a-x)^1$$

$$\frac{dx}{a-x} = k_1 dt \dots \dots \text{eq(ii)}.$$

Integrate eq<sup>o</sup>(ii).

$$\int \frac{dx}{a-x} = k_1 \int dt$$

$$-\log(a-x) = k_1 t + C \dots \text{eq(iii)}.$$

$\hookrightarrow$  Integration Constant.

At initial condition.

when t=0, x=0

$$-\log(a-0) = k_1 \cdot 0 + C$$

$$\therefore \boxed{C = -\log a} \text{ put in eq(iii).}$$

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

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

$$k_1 t = \log_e \frac{a}{a-x}$$

$$k_1 = \frac{2.303 \log_{10} \frac{a}{a-x}}{t}$$

$$\boxed{k_1 = \frac{2.303 \log_{10} \frac{a}{a-x}}{t}} \dots \dots \text{eq(x)}$$

Q.3

For a 1<sup>st</sup> order rxn, the half life period is  $t_{1/2}$ , how much time required for the conversion of 99.9% of initial amount.

Sol.

Relation b/w  $t_{1/2}$  &  $t_{99.9\%}$ .

|                      |                                        |        |
|----------------------|----------------------------------------|--------|
|                      | A (reactant) $\longrightarrow$ product |        |
| at initial ( $t=0$ ) | a mol = 100%                           | 0      |
| after time ( $t$ )   | $(a-x)$ mol = $(100-99.9)\%$           | 99.9 % |

Given: half life =  $t_{1/2}$ ,  $t_{99.9} = ?$   
for 1<sup>st</sup> order rxn

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

$$\& \text{ also } k_1 = \frac{0.693}{t_{1/2}}$$

$$\therefore \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{99.9\%}} \log \frac{100}{0.1}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{99.9\%}} \log 1000$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{99.9\%}} \log (10)^3$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303 \times 3}{t_{99.9\%}}$$

$$\because \log 10 = 1$$

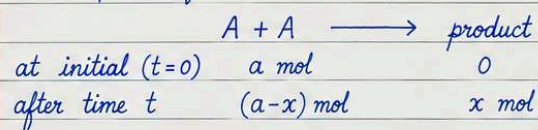
$$t_{99.9\%} = t_{1/2} \times \frac{2.303 \times 3}{0.693}$$

$$\boxed{t_{99.9\%} = t_{1/2} \times 10}$$

Q.4 Deduce an expression for rate constant of second order reaction when both reactants have same concentration.

When both the reactants are same :-

These rx<sup>n</sup> in which the rate not depends upon the second power of reactant conc.



for 2<sup>nd</sup> order rx<sup>n</sup> -

$$\text{rate } (x) \propto [A]^2 \quad r = -\frac{d[A]}{dt} \propto [A]^2$$

$$r = k_2 (a-x)^2 = -\frac{d[A]}{dt} \propto (a-x)^2 \quad \dots \text{eq(i)}$$

$$= -\frac{d[A]}{dt} = k_2 (a-x)^2 \quad \dots \text{eq(i)}$$

$$\text{rate } (x) = -\frac{d[A]}{dt} \propto [A]^2$$

$$r = k_2 [A]^2 = k_2 (a-x)^2 \quad \dots \text{eq(iii)}$$

$$\therefore k_2 = \frac{1}{(a-x)^2} \cdot \frac{dx}{dt} \quad \dots \text{eq(iii)}$$

$$\frac{1}{a-x} = k_2 t + C \quad \dots \text{eq(iii)}$$

↳ Integration cont.

At initial condition

when  $t=0$ ,  $x=0$  (put in eq iii).

$$\frac{1}{a-0} = k_2 \cdot 0 + C$$

$$C = \frac{1}{a} \quad \text{put in eq(iii)}$$

$$\therefore \frac{1}{a-x} = k_2 t + \frac{1}{a} \quad \dots \text{eq(iv)}$$

$$\text{Let } (a-x) = t$$

$$-dx = dt$$

$$dx = -dt$$

on putting the value

$$-\int \frac{dt}{t^2}$$

$$-\int t^{-2} dt \therefore \int x^n dx = \frac{x^{n+1}}{n+1}$$

$$-\left[ \frac{t^{-2+1}}{-2+1} \right]$$

$$t^{-1} \Rightarrow \frac{1}{t} = \frac{1}{a-x}$$

On comparing this eq<sup>n</sup> with  $Y = mx + c$

$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$

$$\frac{1}{a-x} - \frac{1}{a} = k_2 t$$

$$\frac{a-a+x}{a(a-x)} = k_2 t$$

$$\frac{x}{a(a-x)} = k_2 t$$

$$k_2 = \frac{x}{at(a-x)} \quad \dots \text{eq(v)}$$

↳ Integrated rate eqn.

Q.5 A second order reaction in which the initial concentrations of both the reactants are same is 25% complete in 600 sec. How long will it take for the reaction to go to 75% completion?

Solution. For a second order reaction

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

For the first case,  $x = \frac{25}{100} a = 0.25 a$

$t = 600 \text{ sec.}$

$$\begin{aligned} \therefore k &= \frac{1}{200} \times \frac{0.25a}{a(a-0.25a)} \\ &= \frac{1}{600} \times \frac{0.25}{0.75a} = \frac{1}{1800a} \end{aligned}$$

For the second case,  $x = \frac{75}{100} a = 0.75a$

$t = \text{To be calculated}$

$$\begin{aligned} \therefore k &= \frac{1}{t} \times \frac{0.75a}{a(a-0.75a)} \\ &= \frac{1}{t} \times \frac{0.75a}{0.25a} = \frac{3}{ta} \end{aligned}$$

But  $k = \frac{1}{1800a}$  (from the first case)

$$\therefore \frac{1}{1800a} = \frac{3}{ta}$$

$$t = 3 \times 1800 = 5400 \text{ sec.}$$

## Q.6 Effect of temp on Rx<sup>n</sup> Rate & temp. Coefficient of Rx<sup>n</sup> Rate :-

- (i). The rate of rx<sup>n</sup> increases with increasing the temp. (due to increasing kinetic energy of molecule.)  
i.e.  $\text{rate (r)} \propto \text{temp}$  (in general).
- (ii). In case of enzymatic rx<sup>n</sup> (biological rx<sup>n</sup>). the rate of rx<sup>n</sup> increases upto maximum 40°C & then stop or slow due to denaturation of protein.
- (iii). The rate of rx<sup>n</sup> in case of gaseous rx<sup>n</sup> increases 2 to 3 times by increasing 10°C temp. (generally 25°C to 35°C).

$$\frac{r_2}{r_1} = \frac{K_{(25+10)}}{K_{25}}$$

$$\therefore r_2 = (2-3) \text{ times of } r_1.$$

### (iv). Temp. Coefficient :-

The ratio of rate constant of a Rx<sup>n</sup> at 2 different temp. separated by 10°C (usually 25°C to 35°C)

$$\text{Temp. Coeff.} = \frac{K_{(25+10)^\circ\text{C}}}{K_{25^\circ\text{C}}}$$

Q.7 What is Arrhenius equation? How is energy of activation is determined with its help?

(i) Arrhenius equation :-

The Arrhenius equation gives the quantitative relationship between the rate constant ( $k$ ) of a reaction and the absolute temperature ( $T$ ). It is given by

$$k = A e^{-\frac{E_a}{RT}}$$

where,  $k$  = rate constant of the reaction

$A$  = Arrhenius or frequency factor (pre-exponential factor)

$E_a$  = energy of activation ( $\text{J mol}^{-1}$ )

$R$  = universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T$  = absolute temperature ( $\text{K}$ )

(iii) Determination of energy of activation :-

Taking natural logarithm on both sides of the Arrhenius equation,

$$\ln k = \ln A - \frac{E_a}{RT} \quad \dots (i)$$

This equation can be written in the form

$$\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right) \quad \dots (iii)$$

On plotting a graph between  $\ln k$  ( $y$ -axis) and  $\frac{1}{T}$  ( $x$ -axis), a straight line is obtained with slope =  $-\frac{E_a}{R}$  and intercept =  $\ln A$ .

Therefore, the energy of activation is calculated from the slope of the straight line as

$$E_a = -(\text{slope}) \times R$$

Q.8

## Explain the postulate of Collision theory.

### Introduction :-

Collision theory explains the rate of a chemical reaction on the basis of collisions between the reacting molecules (or ions). According to this theory, a chemical reaction occurs only when the reacting particles collide with each other in a proper manner.

### Postulates of Collision Theory :-

- 1 Reaction by collision :- The reacting molecules must collide with each other for a reaction to take place. Without collision, no reaction can occur.
- 2 Effective collision :- Not all collisions are effective. Only those collisions in which the molecules have sufficient kinetic energy (equal to or greater than the activation energy,  $E_a$ ) and proper orientation lead to a chemical reaction.
- 3 Energy requirement :- The colliding molecules must possess a minimum amount of kinetic energy called the activation energy ( $E_a$ ) for the reaction to occur.
- 4 Proper orientation :- The colliding molecules must have the correct orientation so that the chemical bonds can break and new bonds can be formed.
- 5 Rate of reaction :- The rate of a reaction is directly proportional to the number of effective collisions per unit time.

### Conclusion :-

Thus, according to collision theory, a chemical reaction takes place only when the reacting molecules collide with sufficient kinetic energy and proper orientation. The rate of reaction depends on the number of such effective collisions.

Q.9

Explain the term phase, component and degree of freedom with  $H_2O$  molecule.

- 1 **Phase :-** A phase is a homogeneous and physically distinct part of a system which is separated from other parts by well defined boundaries. All points in a phase have identical physical and chemical properties.

**Example ( $H_2O$ ) :-** Water can exist in three different phases - solid (ice), liquid (water) and vapour (steam).

- 2 **Component :-** A component is the minimum number of independent chemical species required to express the composition of all the phases in the system. It is also defined as the minimum number of constituents whose concentrations can be varied independently.

**Example ( $H_2O$ ) :-** In the system containing ice, liquid water and water vapour, all the phases are made up of the same chemical species  $H_2O$ . Hence, the number of components ( $C$ ) = 1.

- 3 **Degree of freedom :-** The degree of freedom ( $F$ ) is the number of independent intensive variables (such as temperature, pressure, concentration) that can be changed without altering the number of phases in equilibrium. It is given by Gibbs phase rule -

$$F = C - P + 2$$

For  $H_2O$  system :-  $C = 1$

At triple point (ice + water + vapour,  $P = 3$ )

$$F = 1 - 3 + 2 = 0$$

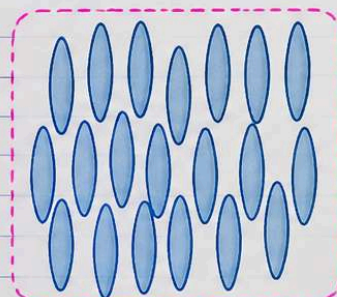
Thus, at triple point of water, the system is invariant ( $F = 0$ ), i.e., temperature and pressure are fixed.

Q.10

Explain the structure and importance of liquid crystals.

#### Structure of liquid crystals :-

- Liquid crystals are a special state of matter which show properties intermediate between solid and liquid.
- Their molecules are usually long, rod-shaped or disc-shaped.
- In liquid crystals, the molecules are arranged in an ordered manner like in a solid, but they can still flow like a liquid.
- They show orientational order (molecules point in a preferred direction) and partial positional order.
- Because of this structure, liquid crystals are anisotropic, i.e., their physical properties (such as refractive index, electrical conductivity, etc.) are different in different directions.



Arrangement of molecules in liquid crystals

#### Importance of liquid crystals :-

- They are widely used in liquid crystal displays (LCDs) in watches, calculators, mobile phones, laptops and television screens.
- They are used in thermometers and temperature sensors.
- They find applications in optical devices, switches and sensors.
- They are also used in research, medical and industrial instruments.

Q.11

Derive the expression for rate constant with the help of collision theory.

The collision theory is based upon the kinetic theory of gases according to which the molecules of a gas are continuously moving and hence colliding with each other. Since for a collision to take place, at least two molecules must be involved, therefore the simple case to consider is that of bimolecular reactions. Hence in the discussion that follows, we shall first discuss the collision theory for bimolecular reactions and then for unimolecular reactions.

Collision theory for bimolecular reactions :

In a bimolecular reaction, in order that two molecules may react, they should not only collide but the collision must be associated with sufficient energy so that the molecules are activated. This means that all collisions are not effective.

The number of effective collisions is only a fraction of the total number of collisions. Taking the specific reaction rate ( $k$ ) as equal to the number of effective collisions per cc per second, if  $Z$  is the number of molecules per cc taking part in the collisions and  $f$  is the fraction of those molecules that are activated, we can write

$$k = Z \times f \quad \dots (i)$$

Now, according to kinetic theory of gases, the fraction of the molecules in a gas possessing energy greater than a particular value  $E$ , is given by the equation

$$f = \frac{\Delta N}{N} = e^{-E/RT} \quad \dots (ii)$$

where  $\Delta N$  = number of molecules possessing energy greater than  $E$   
and  $N$  = total number of molecules.

If  $E$  corresponds to  $E_a$ , the energy of activation, then the fraction of the activated molecules will be given by.

$$f = \frac{\Delta N}{N} = e^{-E_a/RT} \quad \dots (iii)$$

Putting the value of  $f$  from equation (ii) in equation (i), we get

$$k = Z e^{-E_a/RT} \quad \dots (iv)$$

**Q.12 Write the applications of Clausius-Clapeyron equation.**

**Clausius-Clapeyron equation (integrated form) :-**

For the two temperatures  $T_1$  and  $T_2$  with the corresponding vapour pressures  $P_1$  and  $P_2$ , the integrated form of Clausius-Clapeyron equation is

$$\log \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

where,  $\Delta H_{\text{vap}}$  = latent heat of vaporisation

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

$T_1, T_2$  = absolute temperatures (K)

$P_1, P_2$  = vapour pressures at  $T_1$  and  $T_2$

**Applications :-**

**1 Calculation of latent heat of vaporisation :-**

If the vapour pressures at two different temperatures are known, the latent heat of vaporisation can be calculated using Clausius-Clapeyron equation as

$$\Delta H_{\text{vap}} = 2.303 R \frac{\log (P_2/P_1)}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

**2 Calculation of boiling point and freezing point :-**

At the boiling point, the vapour pressure of a liquid is equal to the external pressure (usually 1 atm). Using Clausius-Clapeyron equation, the boiling point (or freezing point) at a given pressure can be calculated when the vapour pressure at another temperature is known.

**3 Calculation of vapour pressure at another temperature :-**

If the vapour pressure ( $P_1$ ) at a temperature  $T_1$  is known, the vapour pressure ( $P_2$ ) at another temperature  $T_2$  can be calculated using

$$\log \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

This helps in finding the vapour pressure of a liquid at any desired temperature.

**4 Calculation of molal depression constant ( $K_f$ ) :-**

The molal depression constant ( $K_f$ ) for a solvent is related to its latent heat of fusion ( $l_f$ ) by the equation

$$K_f = \frac{RT_f^2}{1000 l_f}$$

where,  $K_f$  = molal depression constant ( $\text{K kg mol}^{-1}$ )

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

$T_f$  = normal freezing point of the solvent (K)

$l_f$  = latent heat of fusion per gram of solvent ( $\text{J g}^{-1}$ )

**5 Calculation of molal elevation constant ( $K_b$ ) :-**

The molal elevation constant ( $K_b$ ) for a solvent is related to its latent heat of vaporisation ( $l_v$ ) by the equation

$$K_b = \frac{RT_b^2}{1000 l_v}$$

where,  $K_b$  = molal elevation constant ( $\text{K kg mol}^{-1}$ )

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

$T_b$  = normal boiling point of the solvent (K)

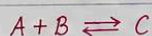
$l_v$  = latent heat of vaporisation per gram of solvent ( $\text{J g}^{-1}$ )

### Q.13 The Le-Chatelier - Brown principle -

For any reaction the physical or chemical equilibrium depends upon various factors like temp., press. and conc. (no. of moles). Therefore, the effect of various parameters (temp., press. and conc.) on eq<sup>m</sup> position was proposed by Le-Chatelier (1885), and F. Brown (1886) which is called as mobile equilibrium or Le-Chatelier and Brown principle. If an equilibrium is subjected to a stress, the equilibrium shifts in such a way as to reduce the stress.

#### 1) Effect of pressure -

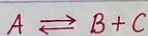
If pressure increases, the reaction move towards those direction where the no. of mol. is less. As -



$$\Delta n = 1 - 2$$

$$\Delta n = -1$$

↑ p  
eq<sup>m</sup> moves  
towards forward  
direction



$$\Delta n = 2 - 1$$

$$\Delta n = +1$$

↑ p  
eq<sup>m</sup> moves in  
backward  
direction

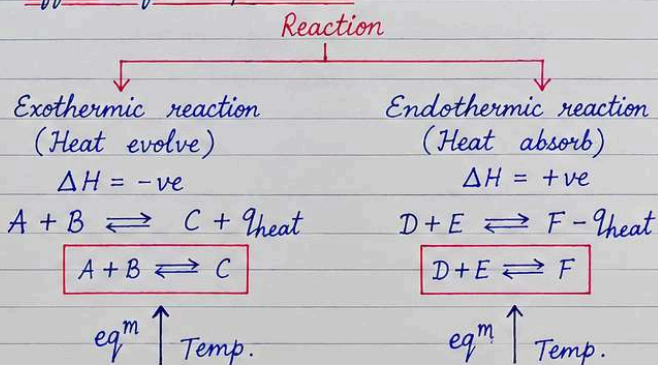


$$\Delta n = 2 - 2$$

$$\Delta n = 0$$

↑ p  
no effect of  
press.  
eq<sup>m</sup> position  
(eq<sup>m</sup> does not change)

#### 2) Effect of temperature :-



- ★ In case of exothermic reaction, when temp. increases, reaction move in backward direction
- ★ In case of endothermic reaction, when temp. increases, reaction move in forward direction.

#### 3) Effect of conc. -

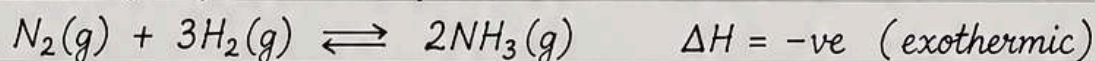
If conc. increases, equilibrium shift towards opposite direction.

Q.14

Discuss the importance of Le Chatelier principle in the manufacture of ammonia by Haber process.

### Haber process :

Ammonia is manufactured by the direct combination of nitrogen and hydrogen according to the reversible reaction :



Le Chatelier principle helps in choosing the suitable conditions to obtain maximum yield of ammonia.

### Importance of Le Chatelier principle :

#### 1 High pressure :

In the reaction, 4 moles of gas ( $1 \text{ N}_2 + 3 \text{ H}_2$ ) give 2 moles of ammonia. By increasing pressure, the equilibrium shifts towards the side with fewer moles, i.e., towards ammonia. Therefore, high pressure (about 200 atm) is used.

#### 2 Moderate temperature :

The reaction is exothermic. According to Le Chatelier principle, lowering the temperature favours the formation of ammonia. But very low temperature makes the reaction rate too slow. Hence, a moderate temperature ( $400-450^\circ\text{C}$ ) is used.

#### 3 High concentration of reactants :

Increasing the concentration (using pure and dry nitrogen and hydrogen) shifts the equilibrium towards ammonia. So excess of reactants is supplied.

#### 4 Removal of product :

Ammonia is continuously removed from the reaction mixture by cooling (liquefaction). This decreases the concentration of ammonia and shifts the equilibrium towards the product side, giving a higher yield.

Thus, Le Chatelier principle is very important in the Haber process because it helps in selecting high pressure, moderate temperature, high concentration of reactants and continuous removal of ammonia to obtain maximum yield.

Question number 15. Write the characteristic of an ideal gas.

- (i) The compressibility factor ( $Z$ ) of an ideal gas is unity i.e.,

$$Z = \frac{PV}{nRT} \Rightarrow 1.$$

- (ii) The product of pressure and volume of an ideal gas is constant temperature. i.e.  $PV = \text{const. at } t = \text{const.}$   
(Boyle's law).

- (iii) If an ideal gas is cooled at constant pressure, its volume decreases continuously till at  $-273^\circ\text{C}$ , its volume becomes zero.

- (iv) If it is allowed to expand without doing any external work, it shows no thermal effect.

- (v) There is no force of attraction between molecules of an ideal gas.

16. Write the characteristic of an real gas.

Real Gases :-

- (i) A real gas does not obey various gas laws particularly at low temperature and high pressure only at high temperature and low pressure, real gas behaves as Ideal Gas.
- (ii) The volume of a real gas does not become zero at  $-273^{\circ}\text{C}$ . i.e., when a gas cooled sufficiently a real gas is suddenly converted into liquid state.
- (iii) The compressibility factor  $Z$  for real gases is not unit, but being less or greater than 1. i.e.,
- $$Z = \frac{P_c V_c}{RT_c}$$
- $$Z = \frac{a}{27b^2} \times \frac{3b}{R \times \left(\frac{8a}{27Rb}\right)}$$
- $$Z = \frac{a}{27b^2} \times \frac{3b \times 27Rb}{8aR}$$
- $$Z = \frac{3}{8} = 0.375$$
- (iv) If it is allowed to expand without doing any external work, it shows no thermal effect.
- (v) There is no force of attraction between molecules of an Ideal Gas.

Q17. Write the postulates of kinetic molecular theory of gases.

Postulates of kinetic molecular theory of Gases :-

The kinetic molecular theory is based on the following assumptions :-

- (i) Gas is made up of small particle / molecule.
- (ii) These molecules are so small that their actual volume is negligible in comparison to the total volume of gas.
- (iii) These molecules are in the state of constant rapid motion in all direction, collide with each other and also with the wall of the container.
- (iv) The molecular collision are perfectly elastic so that there is no loss of energy during the collision with one another or with the wall.
- (v) There is no force of attraction between the molecule or between the molecule and wall.
- (vi) The pressure of gas is due to collision of molecules.
- (vii) Law of classical mechanics are applicable the motion of gaseous molecules.

Q18. Write the average velocity, most probable velocity and root mean square velocity.

(a) **Average Velocity ( $V_a$ ):**— The average velocity is given by the arithmetic mean of the various velocities possessed by the molecule.

i.e. if  $N_1$  molecules have velocity  $V_1$ ,  $N_2$  molecules have velocity  $V_2$  and so on.

Therefore, the average velocity,

$$V_a = \frac{N_1 V_1 + N_2 V_2 + N_3 V_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

Hence, 
$$V_a = \sum_{i=1}^n \frac{N_i V_i}{N_i} \quad \text{--- eq(1).}$$

Thus, the value of  $V_a$  can be determined with the Maxwell's distribution law.

$$\therefore V_a = \sqrt{\frac{8RT}{\pi m}} \quad \text{--- eq(2)}$$

Since, for 1 mole of gas,  $PV = RT$

$$\therefore V_a = \sqrt{\frac{8PV}{\pi m}} \quad \text{--- eq(3)}$$

Since, density ( $d$ ) =  $\frac{m}{V}$

$$\therefore V_a = \sqrt{\frac{8P}{\pi d}} \quad \text{--- eq(4)}$$

(b) **Most probable velocity ( $V_{mp}$ ):**— It is defined as—

"The velocity possessed by the maximum no. of molecules of gas at a given temperature".

From the Maxwell's distribution law, it is given as—

$$V_{mp} = \sqrt{\frac{2RT}{m}} \quad \text{or} \quad \sqrt{\frac{2PV}{m}} = \sqrt{\frac{2P}{d}} \quad \text{--- eq(5)} \quad [\because d = \frac{m}{V}]$$

(c) **Mean square velocity ( $V$ ) and Root mean square velocity ( $V_{rms}$ ):**—

"The mean of the squares of the velocities of all the molecules in the gas, is called mean square velocity [ $V^2$ ]."

i.e. if  $N_1$  molecules have velocity  $V_1$ ,  $N_2$  molecules have velocity  $V_2$  and so on.

The total no. of molecules =  $N_1 + N_2 + \dots = N$

$\therefore$  Kinetic energy of  $N$  gaseous molecules --

$$K.E. = N_1 \times \frac{1}{2} m V_1^2 + N_2 \times \frac{1}{2} m V_2^2 + \dots$$

$$= \frac{1}{2} m (N_1 V_1^2 + N_2 V_2^2 + \dots)$$

$$N V^2 = N_1 V_1^2 + N_2 V_2^2 + \dots$$

$$V^2 = \frac{N_1 V_1^2 + N_2 V_2^2 + \dots}{N} \quad \text{--- eq(6)}$$

This is mean square velocity.

$\therefore$  The root mean square velocity,

$$V_{rms} = \sqrt{N_1 V_1^2 + N_2 V_2^2 + \dots} \quad \text{--- eq(7)}$$

On the basis of kinetic theory of gases—

$$V_{rms} = \sqrt{\frac{3RT}{m}} = \sqrt{\frac{3PV}{m}} = \sqrt{\frac{3P}{d}} \quad \text{--- eq(8)}$$

### Q19. Explain the L-S coupling states.

In light atoms, where the spin-orbit interaction is weak, the electrostatic interaction between the electrons is much stronger than the spin-orbit coupling. In such atoms, the individual orbital angular momenta ( $l$ ) and spin angular momenta ( $s$ ) of all electrons first couple separately to give the resultant orbital angular momentum  $L$  and the resultant spin angular momentum  $S$ . This scheme is known as L-S coupling or Russell-Saunders coupling.

According to L-S coupling, the steps are as follows:—

- (i) The individual orbital angular momenta ( $l_1, l_2, \dots$ ) of all electrons combine vectorially to give the total orbital angular momentum  $L$ .
- (ii) The individual spin angular momenta ( $s_1, s_2, \dots$ ) of all electrons combine vectorially to give the total spin angular momentum  $S$ .
- (iii) The total orbital angular momentum  $L$  and total spin angular momentum  $S$  then couple to give the resultant total angular momentum  $J$ , i.e.  $J = L+S, L+S-1, \dots, |L-S|$ .

The quantum numbers used to describe the L-S coupling states are:

$S$  = total spin quantum number ( $S = 0, 1, 2, \dots$ )

$L$  = total orbital angular momentum quantum number  
( $L = 0, 1, 2, \dots$  corresponding to S, P, D, F, ...)

$J$  = total angular momentum quantum number  
( $J = L+S, L+S-1, \dots, |L-S|$ )

$M_J$  =  $-J, -J+1, \dots, +J$  ( $2J+1$  values)

Each L-S coupling state is denoted by the term symbol  $^{2S+1}L_J$

where  $(2S+1)$  is the multiplicity of the state.

**Q20.** Write the postulate of Werner's theory of coordination complexes.

**Ans.** The main postulates of Werner's theory of coordination complexes are as follows:

1. Metals show two types of valencies: primary and secondary. The primary valencies are ionisable, satisfy themselves by negative ions and are equal to the oxidation state of the metal. The secondary valencies are non-ionisable, satisfy themselves by neutral molecules or anions and are equal to the coordination number of the metal.
2. The primary valencies are directed towards ions outside the coordination sphere, while the secondary valencies are directed towards ligands inside the coordination sphere.
3. Each metal ion has a definite and fixed number of secondary valencies, which is called the coordination number. These secondary valencies are satisfied by a definite number of ligands.
4. The secondary valencies are directional in nature and are satisfied in space in definite geometrical arrangements e.g., octahedral, tetrahedral, square planar, etc.
5. The ligands may be neutral molecules (such as  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ) or negative ions (such as  $\text{Cl}^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ ) and each ligand satisfies one secondary valency of the metal.
6. The group of metal ion and the ligands attached to it by secondary valencies forms a coordination sphere, which remains intact both in solid state and in solution.
7. The ions which satisfy the primary valencies are present outside the coordination sphere and can be ionised in solution.
8. The theory explains the stereoisomerism of coordination complexes on the basis of definite geometrical arrangement of ligands around the central metal atom.

## Q21. Valence BOND Theory (VBT) :-

The theory was developed by Pauling, based on the following assumptions :-

- i) The central metal atom/cation has empty s, p & d atomic orbitals, equal to its co-ordination no. These vacant orbitals hybridised together to form hybrid orbitals of same energy. These hybrid orbitals are vacant, equivalent in energy and have definite geometry.
- ii) The ligands have atleast 1 lone pair of electrons.
- iii) According to VBT, the bonding in complexes arises when a ~~fitted~~ orbital of ligand having lone pair of  $e^-$  overlaps to vacant hybrid orbital of central metal atom and form co-ordinated bond.
- iv) The strong field ligand (CO,  $CN^\ominus$ , en,  $NO^\ominus$ ,  $NH_3^*$ ..... etc.) have the tendency to push and pair up the non-bonding electron present in the atomic orbital of metal ; where as the weak ligand ( $H_2O$ ,  $F^\ominus$ ,  $Cl^\ominus$ ,  $Br^\ominus$ ..... etc.) have no such type of tendency.
- v) The pairing of electrons in the atomic orbital of metal take place according to Hund's Rule.
- vi) If the unpaired electrons are present in the atomic orbital of metal then it is paramagnetic otherwise diamagnetic complex.
- vii) If the ligand is strong field, to form low spin (inner orbital complex), and vice-versa.

Q22. Sidgwick's Concept Of Effective Atomic No. or EAN Rule:

Sidgwick suggested that the total no. of  $e^-$  on the central metal atom in a complex including those gained from ligands in the bonding, is called EAN of central metal ion. In most of the cases the EAN is equal to the atomic no. of next inert gas.

$$\text{EAN} = \text{Atomic No. of Metal Ion} - \text{Electron lost by metal} + \text{Electron gained by ligand} \Rightarrow \text{Next Inert gas.}$$

| Complex                                                                                               | Atom No. of central metal ion<br>(Z) | Oxidation state of central metal atom<br>(X) | No. of $e^-$ gained by ligand<br>$2(y)$ | EAN<br>(Z-X+2-y) | Next Inert gas |
|-------------------------------------------------------------------------------------------------------|--------------------------------------|----------------------------------------------|-----------------------------------------|------------------|----------------|
| $[\text{Fe}(\text{CN})_6]^{3-}$                                                                       | 26                                   | +3                                           | $2 \times 6$                            | 35               | 36(Kr)         |
| $[\text{Cr}(\text{NH}_3)_6]^{3+}$                                                                     | 24                                   | +3                                           | $2 \times 6$                            | 33               | 36(Kr)         |
| $[\text{Ni}(\text{NH}_3)_6]^{2+}$                                                                     | 28                                   | +2                                           | $2 \times 6$                            | 38               | 36(Kr)         |
| $[\text{Pt}(\text{NH}_3)_4]^{2+}$                                                                     | 78                                   | +2                                           | $2 \times 4$                            | 84               | 86(Rn)         |
| $[\text{Ag}(\text{NH}_3)_2]^+$                                                                        | 47                                   | +1                                           | $2 \times 2$                            | 50               | 54(Xe)         |
| $[\text{Co}(\text{en})_3]^{3+}$<br><small>en = 6</small>                                              | 27                                   | +3                                           | $2 \times 6$                            | 36               | 36(Kr)         |
| $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$<br>$\downarrow$<br>$[\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$ | 47                                   | +1                                           | $2 \times 2$                            | 50               | 54(Xe)         |
| $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$                                                             | 24                                   | +3                                           | $2 \times 6$                            | 33               | 36(Kr)         |
| $[\text{Ni}(\text{CO})_4]^0$                                                                          | 28                                   | 0                                            | $2 \times 4$                            | 36               | 36(Kr)         |
| $[\text{Cu}(\text{CN})_4]^{2-}$                                                                       | 29                                   | +2                                           | $2 \times 4$                            | 35               | 36(Kr)         |

Q23. Write the difference between double salt and coordination complexes.

Ans.

| <u>Basis</u>             | <u>Double Salt</u>                                                                                   | <u>Coordination Complexes</u>                                                                                          |
|--------------------------|------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|
| 1. Definition            | Double salts are compounds which on dissolving in water give all the constituent ions independently. | Coordination complexes are compounds in which a central metal atom/ion is surrounded by ligands forming a complex ion. |
| 2. Nature                | They are simple ionic compounds.                                                                     | They are complex compounds with definite coordination sphere.                                                          |
| 3. Existence in solution | In aqueous solution, they dissociate completely into all their constituent ions.                     | In aqueous solution, they retain their complex ion as a whole and do not give free constituent ions.                   |
| 4. Composition           | They show variable composition.                                                                      | They have definite composition and fixed stoichiometry.                                                                |
| 5. Properties            | Their properties are the sum of the properties of the constituent ions.                              | They show new properties different from the constituent ions.                                                          |
| 6. Example               | Mohr's salt<br>$(\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O})$          | $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,<br>$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ etc.                              |

## Q24. Write a short note on ligands.

Any species having (+ve)  $[N \equiv O^+]$ , (-ve) or neutral charge which have capability to donate the lone pair of electrons to the vacant d-orbital of metal in a complex, are called ligands. Ligands act as Lewis base.

### Types of Ligands : —

Ligands are classified into the following category on the basis of donor atom present in them : —

i) Monodentate : — Ligands which donate one lone pair of electrons to the metal atom, are known as monodentate.

for eg :-  $CN^-$ ,  $Cl^-$ ,  $Br^-$ ,  $OH^-$ ,  $CH_3COO^-$  (pyridine)  
 $:CO$ ,  $NO^+$ ,  $H_2O$ ,  $NH_3$ ,  $CH_3-NH_2$ , 

ii) Ambidentate : — It is monodentate but have two types of donor atom.

for eg :-  $CN^-$ ,  $NO_2^-$ ,  $SCN^-$

|                                       |                                          |                                    |
|---------------------------------------|------------------------------------------|------------------------------------|
| $\leftarrow : C \equiv N :$<br>cyano. | $-C \equiv N : \rightarrow$<br>Isocyano. | $\leftarrow : NO_2$<br>Nitro (N).  |
| $\leftarrow : SCN :$<br>Thiocyanato.  | $\leftarrow : NCS :$<br>Isothiocyanato.  | $\leftarrow : ONO$<br>Nitrito (O). |

## Q25. Write the different type of structural isomerism with example.

Isomers which have the same molecular formula but different structural arrangement of atoms are called structural isomers. These are of the following types :-

- 1. Ionisation isomerism** :- This type of isomerism occurs due to exchange of groups between the complex ion and ion outside it. Such compounds behave differently when dissolved in water.

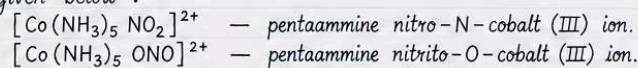
**Example** :-  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  is red-violet in solution and gives a precipitate with  $\text{BaCl}_2$ , confirming the presence of  $\text{SO}_4^{2-}$  ion.

On the other hand,  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  is red and does not give test for sulphate ion in solution but instead gives precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$ . These two compounds are ionisation isomers.

- 2. Hydrate isomerism** :- These isomers differ in number of water molecules attached to metal ion as ligands. Thus three isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  are known as given below. From the conductivity measurement and quantitative precipitation of ionized chlorine, they have the following formulae :-

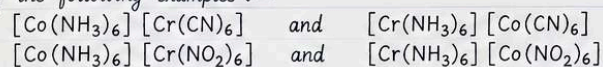
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  — Violet (three ionic chlorine)
- $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  — Green (two ionic chlorine)
- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  — Dark green (one ionic chlorine)

- 3. Linkage isomerism** :- This type of isomerism occurs when more than a single atom in a coordinated group may act as a donor. For example, in  $\text{NO}_3^-$  ion, either oxygen or nitrogen can act as a donor giving two different isomers. Two isomers of cobalt having ligands ammonia and  $\text{NO}_2$  showing linkage isomerism are given below :-



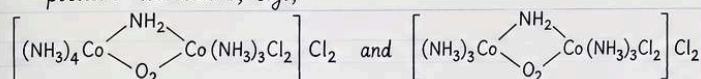
Another ligand which can exhibit linkage isomerism is thiocyanate ion  $\text{SCN}^-$ , e.g., it can form  $\text{M-SCN}$  and  $\text{M-NCS}$ .

- 4. Coordination isomerism** :- When both positive and negative ions are complex, isomerism is possible due to the interchange of ligands between the two complex ions. This type of isomerism is called coordination isomerism and is illustrated by the following examples :-



In  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is a cation and  $[\text{Cr}(\text{CN})_6]^{3-}$  is an anion. Ligands interchange their positions to form  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ . Cation is written first.

- 5. Coordinate position isomerism** :- In polynuclear complexes, an interchange of ligands between two metal atoms gives rise to another type of isomerism called coordinate position isomerism, e.g.,



Tetramminecobalt (III)  $\mu$ -amido- $\mu$ -superoxodiamminedichloridocobalt (III) chloride and triamminedichloridocobalt (III)  $\mu$ -amido- $\mu$ -superoxotriamminechloridocobalt (III) are coordinate position isomers. Here  $\text{O}_2$ , superoxo, is one bridging group and the other is amido ( $\text{NH}_2$ ).

- 6. Polymerization isomerism** :- This is not a true isomerism since it occurs between compounds having the same empirical formula but different molecular formula. Thus  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]_n$ ,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  have same empirical formula but have molecular weight in the ratio of 1:2.

## Q27. Explain the collision diameter and collision number.

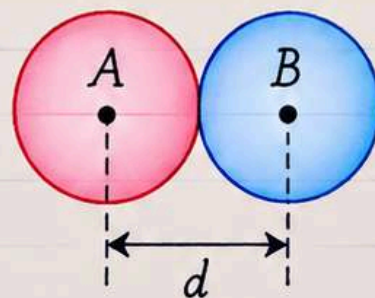
### 1. Collision diameter :-

Collision is an event in which the centres of two identical molecules come within a distance  $\sigma$  from one another as shown in the figure below.

Sigma ( $\sigma$ ), which is the distance between centres of the molecules at the point of closest approach, is called the collision diameter.

The collision diameter ( $d$ ) is the minimum distance between the centres of two reacting molecules at the instant of collision, at which they just touch each other. It is equal to the sum of the radii of the two molecules.

$$d = r_A + r_B$$



### 2. Collision number :-

The collision number ( $Z$ ) is the total number of collisions occurring per second between the molecules in a unit volume of the reaction mixture.

$$Z = \sqrt{2} \pi \sigma^2 \bar{c} \rho$$

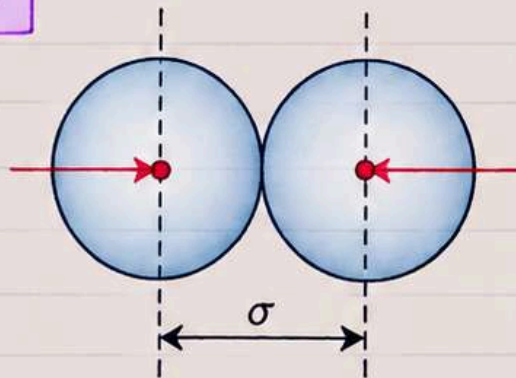
where,

$Z$  = Collision number

$\sigma$  = Diameter of molecule (collision diameter)

$\bar{c}$  = Average velocity of the molecules

$\rho$  = Number of molecules per unit volume of the gas (density).



### (iii) Collision frequency

It is the number of molecular collisions occurring per unit time per unit volume of the gas.

Total number of molecules colliding per unit volume per unit time is obtained by multiplying collision number by number density  $\rho$ . Thus total number of colliding molecules  $= \sqrt{2} \pi \sigma^2 \bar{c} \rho^2$ .

Since each collision involves two molecules of the same type, number of collisions is given by one half of this

$$\begin{aligned} Z_{11} &= \frac{1}{2} \cdot \sqrt{2} \pi \sigma^2 \bar{c} \rho^2 \\ &= \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{c} \rho^2 \end{aligned} \quad \dots(ii)$$

It readily follows that number of collisions of molecules of type 1 with those of type 2 would be given by

$$Z_{12} = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{c} \rho_1 \rho_2 \quad \dots(iii)$$

where  $\rho_1$  and  $\rho_2$  are densities of molecules of type 1 and 2 respectively.

### (iv) Mean Free Path

Mean free path ( $\lambda$ ) is defined as the mean distance travelled by a gas molecule between two successive collisions. Thus

$$\lambda = \frac{\bar{c}}{Z_1} = \frac{\bar{c}}{\sqrt{2} \pi \sigma^2 \bar{c} \rho} \quad [\text{Substituting from (i)}] \quad \dots(iv)$$

$$\text{Also } PV = nRT = nN_A kT$$

where  $N_A$  = Avogadro's number  
and  $k$  = Boltzmann constant

[Gas constant ( $R$ ) = Avogadro's no. ( $N_A$ )  $\times$  Boltzmann constant]

$$\text{or } P = \frac{nN_A kT}{V} = \frac{NkT}{V} \quad \text{where } N (= nN_A) \text{ is total no. of molecules in } n \text{ moles of the gas}$$

Since  $\rho$  is the number of molecules per unit volume,  $\rho = \frac{N}{V}$

$$\text{Thus } P = \rho kT \quad \text{or} \quad \rho = \frac{P}{kT} \quad \dots(v)$$

Substituting the value of  $\rho$  of in (iv)

$$\lambda = \frac{kT}{\sqrt{2} \pi \sigma^2 P}$$

Mean free path is also related to the viscosity of the gas.

It is given by the equation

$$\lambda = \eta \sqrt{\frac{3}{Pd}}$$

where  $P$  = Pressure of the gas  
 $d$  = Density of the gas  
 $\eta$  = coefficient of viscosity of the gas

### Q28. (iii) Collision frequency

It is the number of molecular collisions occurring per unit time per unit volume of the gas.

Total number of molecules colliding per unit volume per unit time is obtained by multiplying collision number by number density  $\rho$ . Thus total number of colliding molecules

$$= \sqrt{2} \pi \sigma^2 \bar{c} \rho^2.$$

Since each collision involves two molecules of the same type, number of collisions is given by one half of this

$$\begin{aligned} Z_{11} &= \frac{1}{2} \cdot \sqrt{2} \pi \sigma^2 \bar{c} \rho^2 \\ &= \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{c} \rho^2 \end{aligned} \quad \dots (ii)$$

It readily follows that number of collisions of molecules of type 1 with those of type 2 would be given by

$$Z_{12} = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{c} \rho_1 \rho_2 \quad \dots (iii)$$

where  $\rho_1$  and  $\rho_2$  are densities of molecules of type 1 and 2 respectively.

### Q28. (iv) Mean Free Path.

Mean free path ( $\lambda$ ) is defined as the mean distance travelled by a gas molecule between two successive collisions. Thus

$$\lambda = \frac{\bar{c}}{Z_1} = \frac{\bar{c}}{\sqrt{2} \pi \sigma^2 \bar{c} \rho} \quad [\text{Substituting from (i)}] \quad \dots (iv)$$

Also  $PV = nRT = nN_A kT$   
where  $N_A$  = Avogadro's number  
and  $k$  = Boltzmann constant

[Gas constant ( $R$ ) = Avogadro's no. ( $N_A$ )  $\times$  Boltzmann constant]

$$\text{or } P = \frac{nN_A kT}{V} = \frac{NkT}{V} \quad \text{where } N (= nN_A) \text{ is total no. of molecules in } n \text{ moles of the gas}$$

Since  $\rho$  is the number of molecules per unit volume,  $\rho = \frac{N}{V}$   
Thus  $P = \rho kT$  or  $\rho = \frac{P}{kT} \quad \dots (v)$

Substituting the value of  $\rho$  of in (iv)

$$\lambda = \frac{kT}{\sqrt{2} \pi \sigma^2 P}$$

Mean free path is also related to the viscosity of the gas. It is given by the equation

$$\lambda = \eta \sqrt{\frac{3}{Pd}}$$

where  $P$  = Pressure of the gas  
 $d$  = Density of the gas  
 $\eta$  = coefficient of viscosity of the gas

## Q29. Derive the Clausius-Clapeyron equation.

### Introduction :-

The Clausius-Clapeyron equation gives the relation between the vapour pressure of a substance and temperature during a phase change (liquid  $\Rightarrow$  vapour). It helps to calculate the enthalpy (latent heat) of vaporization or sublimation and to find how vapour pressure changes with temperature.

### Derivation :-

Consider a system in which a liquid and its vapour are in dynamic equilibrium at a certain temperature  $T$  and pressure  $P$ .

- 1 **Clapeyron equation** :- For a phase change, the slope of the equilibrium curve on a  $P$ - $T$  diagram is given by the Clapeyron equation :

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad \dots (1)$$

where,

$\Delta H$  = enthalpy change for the phase change

$T$  = absolute temperature

$\Delta V$  = change in molar volume ( $V_2 - V_1$ )

- 2 **For liquid-vapour equilibrium** :- For vaporization of a liquid,

$\Delta H = \Delta H_{\text{vap}}$  (molar enthalpy of vaporization)

$\Delta V = V_g - V_l$

Hence, equation (1) becomes

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T(V_g - V_l)} \quad \dots (2)$$

### 3 Approximations :-

- ii Volume of the liquid ( $V_l$ ) is very small as compared to the volume of the vapour ( $V_g$ ), hence  $V_g - V_l \approx V_g$ .
- iii The vapour behaves as an ideal gas, so for 1 mole,

$$V_g = \frac{RT}{P}$$

where,  $R$  = gas constant.

Substituting in equation (2), we get

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}} P}{RT^2} \quad \dots (3)$$

- 4 **Integration** :- Assuming  $\Delta H_{\text{vap}}$  remains constant over the temperature range, integrate equation (3) between two temperatures  $T_1$  and  $T_2$  with corresponding vapour pressures  $P_1$  and  $P_2$ .

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

Integrating, we get

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left[ -\frac{1}{T} \right]_{T_1}^{T_2}$$

$$\ln \left( \frac{P_2}{P_1} \right) = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

This is the Clausius-Clapeyron equation.

## Q30. Explain the Orgel diagram for $D^1$ metal ion with example.

### Introduction :-

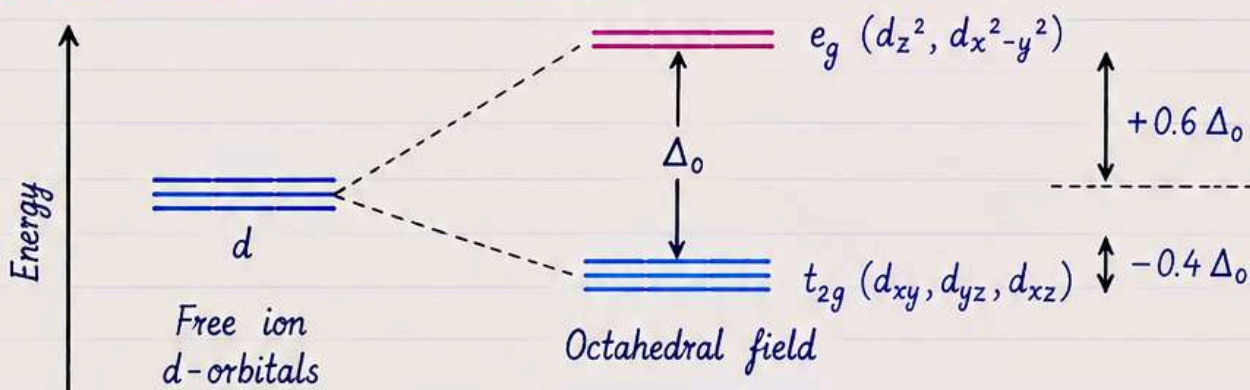
The Orgel diagram is a qualitative energy level diagram which shows the splitting of d-orbitals of a transition metal ion in an octahedral crystal field and the possible electronic transitions between these levels.

For a  $D^1$  configuration, there is one electron in the d-orbitals. In an octahedral field, the five d-orbitals split into two sets: lower energy  $t_{2g}$  ( $d_{xy}, d_{yz}, d_{xz}$ ) and higher energy  $e_g$  ( $d_{z^2}, d_{x^2-y^2}$ ).

### 1 Splitting of d-orbitals in octahedral field :-

- The three  $t_{2g}$  orbitals ( $d_{xy}, d_{yz}, d_{xz}$ ) are stabilized by an amount  $0.4 \Delta_o$  (lower in energy).
- The two  $e_g$  orbitals ( $d_{z^2}, d_{x^2-y^2}$ ) are destabilized by an amount  $0.6 \Delta_o$  (higher in energy).
- The energy separation between  $t_{2g}$  and  $e_g$  levels is  $\Delta_o$  (octahedral crystal field splitting).

### 2 Orgel diagram for $D^1$ metal ion :-



### 3 Electronic transitions :-

- In a  $D^1$  system, the single electron occupies the lower  $t_{2g}$  level in the ground state:  $t_{2g}^1 e_g^0$ .
- When light is absorbed, the electron can be excited from  $t_{2g}$  to  $e_g$  level, giving one spin-allowed transition:



### 4 Example :-

$Ti^{3+} (d^1)$  in an octahedral complex such as  $[Ti(H_2O)_6]^{3+}$ .

- Ground state configuration:  $t_{2g}^1 e_g^0$ .
- It shows one absorption band in the visible region corresponding to the transition  $t_{2g} \rightarrow e_g$  ( $\Delta_o$ ).

**Q31.**

**Explain the splitting of d orbital in octahedral complexes according to CFT.**

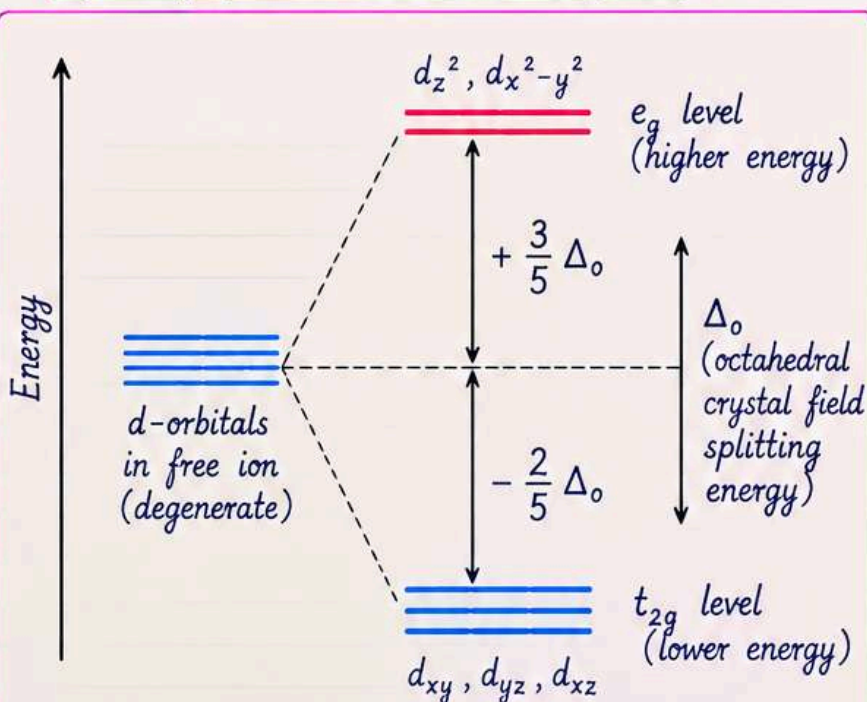
**Octahedral complex :-**

In an octahedral complex, the central metal ion is surrounded by six ligands placed at the corners of an octahedron along the x, y and z axes.

**Reason for splitting :-**

- In a free metal ion, the five d-orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_z^2$ ,  $d_{x^2-y^2}$ ) are degenerate (same energy).
- When ligands approach along the three axes, their negative charge repels the electrons in the d-orbitals.
- Orbitals pointing directly towards the ligands experience greater repulsion and are raised in energy, while orbitals lying between the axes experience less repulsion and are lowered in energy.

**Splitting pattern in octahedral field :-**



Splitting of d-orbitals in an octahedral complex

**Groups of orbitals :-**

**1  $t_{2g}$  orbitals (lower energy) :-**  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$

- These orbitals lie between the ligand axes.
- They experience less repulsion and are stabilized.
- Their energy is lowered by  $\frac{2}{5} \Delta_o$  relative to the average energy.

**2  $e_g$  orbitals (higher energy) :-**  $d_z^2$ ,  $d_{x^2-y^2}$

- These orbitals point directly towards the ligands.
- They experience greater repulsion and are destabilized.
- Their energy is raised by  $\frac{3}{5} \Delta_o$  relative to the average energy.

**Important points :-**

- The energy separation between  $t_{2g}$  and  $e_g$  levels is  $\Delta_o$  (octahedral crystal field splitting energy).
- $t_{2g}$  set contains 3 orbitals and  $e_g$  set contains 2 orbitals.
- Average energy of the five d-orbitals remains the same (barycentre).
- Each electron in  $t_{2g}$  lowers the energy by  $\frac{2}{5} \Delta_o$  and each electron in  $e_g$  raises the energy by  $\frac{3}{5} \Delta_o$ .

Q32.

Explain the combined  $D^1$  and  $D^9$  Orgel energy level diagram for octahedral complexes.

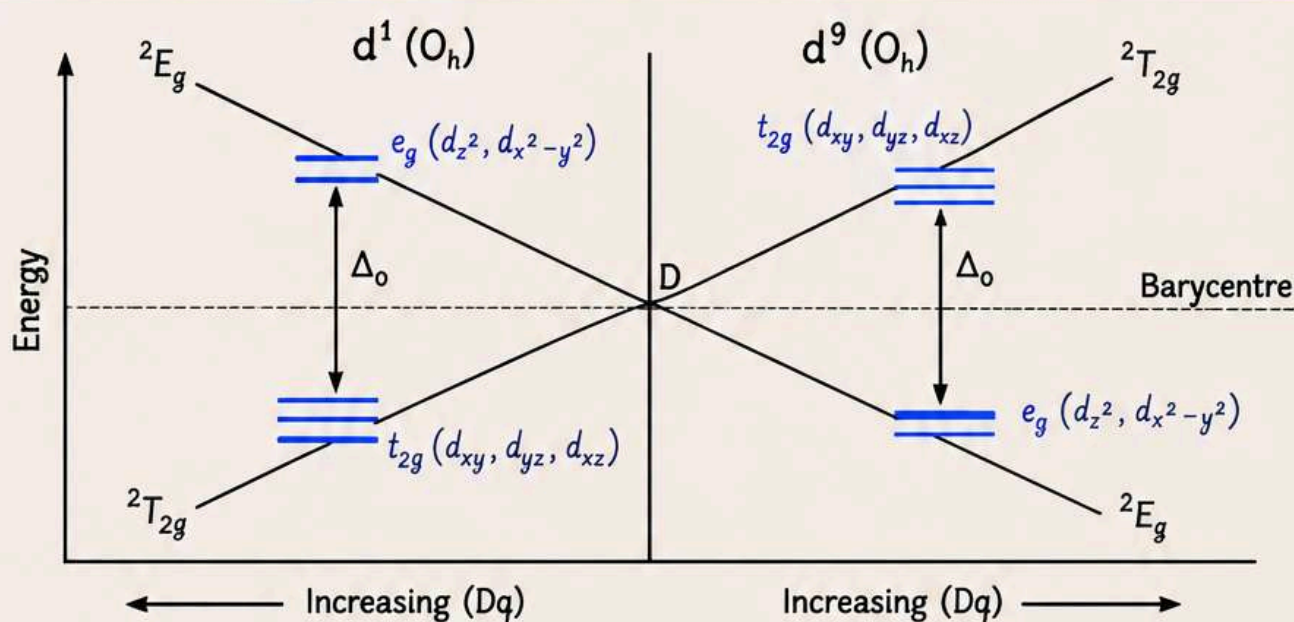
### 1. Orgel diagram :-

The plot of variation of energy level of spectroscopic states with crystal field strength ( $Dq$ ) is called an Orgel diagram. The energy level diagrams for  $d^1$  and  $d^9$  in an octahedral field ( $O_h$ ) are mirror images of each other and can be combined in a single diagram.

### 2. Splitting of d-orbitals in octahedral field :-

- In an octahedral field, the five d-orbitals split into two sets: lower energy  $t_{2g}$  ( $d_{xy}, d_{yz}, d_{xz}$ ) and higher energy  $e_g$  ( $d_{z^2}, d_{x^2-y^2}$ ).
- The energy separation between these two sets is  $\Delta_o$  ( $= 10 Dq$ ).

### 3. Combined Orgel energy level diagram for $d^1$ and $d^9$ :-



### 4. Explanation :-

- Left side of the diagram shows the energy levels for a  $d^1$  ion.
- In  $d^1$  configuration, the single electron occupies the lower  $t_{2g}$  level ( $2T_{2g}$ ) and can be excited to the higher  $e_g$  level ( $2E_g$ ) (spin-allowed transition).
- Right side shows the energy levels for a  $d^9$  ion.
- In  $d^9$  configuration, the single hole (unpaired electron) lies in the higher  $e_g$  level ( $2E_g$ ) and can be excited to the lower  $t_{2g}$  level ( $2T_{2g}$ ).
- Thus, the diagrams for  $d^1$  and  $d^9$  are symmetrical about the barycentre and give similar spectral patterns.

Q33.

Explain the  $L - S$  coupling/spin-orbit coupling.

### C. Spin-orbital or $L - S$ Coupling

The magnetic effects of the resultant angular momentum,  $L$  and the resultant spin moment  $S$  couple together to give new quantum number  $J$  called the **total angular quantum number**.  $J$  values can be obtained by the vectorial combination of  $L$  and  $S$  by the coupling scheme called **Russell Saunders or LS coupling**. The  $J$  can acquire all quantized positive values in the range  $|L - S|$  to  $L + S$  as :

$$J = (L + S), (L + S - 1), (L + S - 2) \dots \dots \dots |L - S|$$

The  $J$  values are separated by 1. The modulus sign  $| |$  indicates the absolute value of  $|L - S|$  so that  $J \geq 0$ .

The  $J$  value is written as a subscript in the term symbol.

We shall illustrate these rules by taking the examples of  $p^2$  and  $d^2$  configurations :

#### $p^2$ -Configuration

##### Step 1

For the two  $p$ -electrons  $l_1 = 1$  and  $l_2 = 1$

$$\begin{array}{lll} L & = & (1 + 1), \quad (1 + 1 - 1), \quad (1 + 1 - 2) \\ & = & 2, \quad 1, \quad 0 \\ \text{States} & D, & P, \quad S \end{array}$$

It may be noted that the last value of  $L$  can also be obtained by  $|l_1 - l_2|$  i.e.  
 $1 - 1 = 0$

The energy states are  $S$ ,  $P$  and  $D$ .

##### Step 2

For two electrons,

$$\begin{array}{ll} L & = \quad \left(+\frac{1}{2} + \frac{1}{2}\right), \quad \left(+\frac{1}{2} + \frac{1}{2} - 1\right), \\ & = \quad 1, \quad 0 \end{array}$$

It may be noted that the second value of  $S$  can also be obtained by  $|s_1 - s_2|$  or  $\frac{1}{2} - \frac{1}{2} = 0$

The spin multiplicity  $(2S + 1)$  is :

For  $S = 1$ , spin multiplicity = 3 (Triplet)

For  $S = 0$ , spin multiplicity = 1 (Singlet)

Therefore, we have six states corresponding to states  $D$ ,  $P$  and  $S$  and corresponding to spin multiplicity 3 and 1 each which can be written as

$$^3S, ^3P, ^3D, ^1S, ^1P \text{ and } ^1D.$$

##### Step 3

Calculation of  $J$  values;

(a) When  $L = 2, 1$  and  $0$  and  $S = 1$

(i) When  $L = 2, S = 1$  i.e.  $^3D$  state

$$\begin{aligned} J &= (2 + 1), & (2 + 1 - 1), & (2 + 1 - 2) \\ &= 3, & 2, & 1 \end{aligned}$$

We cannot have  $J = 0$  because the range  $J$  is from  $|L + S|$  to  $|L - S|$  i.e.  $|2 + 1|$  to  $|2 - 1|$  i.e. 3 to 1

$\therefore$  Complete spectroscopic term symbols  $^{2S+1}L_J$   
 $^3D_3, ^3D_2$  and  $^3D_1$ .

(ii) When  $L = 1$  and  $S = 1$  i.e.  $^3P$  state.

$$\begin{aligned} J &= (1 + 1), & (1 + 1 - 1), & (1 + 1 - 2) \\ &= 2, & 1, & 0 \end{aligned}$$

$\therefore$  Complete spectroscopic terms are :

$$^3P_2, ^3P_1 \text{ and } ^3P_0.$$

(iii) When  $L = 0$  and  $S = 1$  i.e.  $^3S$  state

$$\begin{aligned} J &= 1 + 0 \\ &= 1 \end{aligned}$$

We cannot have  $J = 0$  because the range for  $J$  is from  $|L + S|$  to  $|L - S|$  i.e.  $|0 + 1|$  to  $|0 - 1|$  i.e. 1 only

Complete spectroscopic term symbol  $^{2S+1}L_J$  is  $^3S_1$

(b) When  $L = 2, 1$  and  $0$  and  $S = 0$

(i) When  $L = 2$  and  $S = 0$  i.e.  $^1D$  states

$$\begin{aligned} J &= 2 + 0 \\ &= 2 \end{aligned}$$

$J$  cannot have values 1 and 0 because the range is from  $|2 + 0|$  to  $|2 - 0|$  i.e. 2 only

$\therefore$  Complete spectroscopic term symbol,  $^{2S+1}L_J$  is  $^1D_2$

(ii) When  $L = 1$  and  $S = 0$  i.e.  $^1P$  states

$$\begin{aligned} J &= 1 + 0 \\ &= 1 \end{aligned}$$

$J$  cannot have the value 0 because  $J$  ranges between  $|1 + 0|$  and  $|1 - 0|$  i.e. 1 only

$\therefore$  Complete spectroscopic term is  $^1P_1$ .

(iii) When  $L = 0$  and  $S = 0$  i.e.  $^1S$  state

$$J = 0$$

$\therefore$  Complete spectroscopic term is  $^1S_0$

Thus, the total term symbols for  $p^2$  configuration are :

$$^3D_3, ^3D_2, ^3D_1, ^3P_2, ^3P_1, ^3P_0, ^3S_1, ^1D_2, ^1P_1 \text{ and } ^1S_0.$$

Each of these value corresponds to an electronic arrangement.

**Q34.****Short note on Jahn-Teller distortion****Introduction**

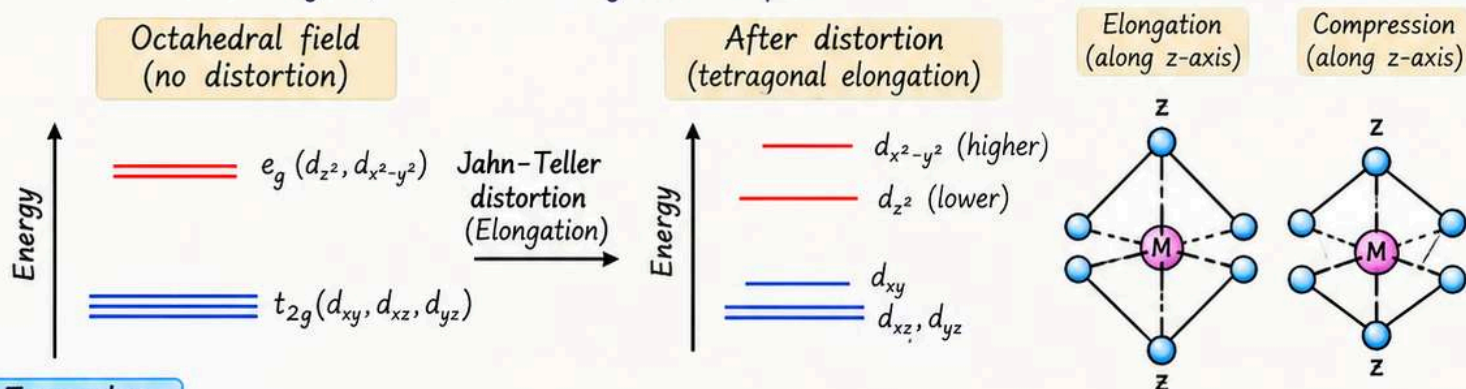
Jahn-Teller distortion is a geometric distortion that occurs in certain non-linear molecular complexes when the ground electronic state is degenerate. It was explained independently by Hermann Jahn and Edward Teller in 1937. The distortion removes the degeneracy and lowers the total energy of the complex, making it more stable.

**Statement of Jahn-Teller Theorem**

"Any non-linear molecule or complex ion in a degenerate electronic state will undergo a distortion that removes the degeneracy and lowers the overall energy."

**In Octahedral Complexes**

- In an ideal octahedral field, the five d-orbitals split into two sets:  $t_{2g}$  (lower energy) and  $e_g$  (higher energy), which are degenerate within each set.
- If the electronic configuration leads to an uneven occupation of the degenerate  $e_g$  orbitals (e.g.,  $d^4$  (high spin),  $d^9$ , etc.), the complex becomes unstable.
- To remove the degeneracy, the octahedron distorts, usually by an elongation or compression along one of the axes (commonly the z-axis).
- This distortion changes the energies of the d-orbitals, making one orbital lower in energy and the other higher, thus stabilizing the complex.

**Examples**

- $d^4$  high-spin complexes: e.g.,  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- $d^9$  complexes: e.g.,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- Also seen in some  $d^7$  (high spin) octahedral complexes.

**Conclusion**

Jahn-Teller distortion removes the degeneracy of electronic states in non-linear complexes, leading to a lower energy and more stable structure. It is commonly observed in octahedral complexes having an uneven occupancy of  $e_g$  orbitals, resulting in a tetragonal distortion (elongation or compression) along one axis.

**Q35.** Critical constant by the Vander-Waal's Eq<sup>n</sup>:-

To solve the vander-waal's eq<sup>n</sup>:-

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \quad \text{----- (1)}$$

It is the eq<sup>n</sup>. for 1 mol of real gas.

$$\left( PV - Pb + a - \frac{ab}{V^2} \right) = RT$$

$$\text{i.e., } PV^3 - PV^2b + aV - ab = RTV^2 \quad \text{----- (2)}$$

$$V^3 - V^2b + aV - \frac{ab}{P} = \frac{RT}{P} V^2$$

$$\text{i.e., } V^3 - V^2 \left( b + \frac{RT}{P} \right) + \frac{a}{P} V - \frac{ab}{P} = 0 \quad \text{----- (3)}$$

At critical temp. & press.,

$$P = P_c, \quad T = T_c$$

eq<sup>n</sup>. (3) becomes—

$$V^3 - \left( b + \frac{RT_c}{P_c} \right) V^2 + \frac{a}{P_c} V - \frac{ab}{P_c} = 0 \quad \text{----- (4)}$$

When,  $T = T_c$ ,  $P = P_c$  then  $V = V_c$

$$\therefore V_c^3 - \left[ b + \frac{RT_c}{P_c} \right] V_c^2 + \frac{aV_c}{P_c} - \frac{ab}{P_c} = 0 \quad \text{--- (5)}$$

As;  $V = V_c \Rightarrow V - V_c = 0$

$$(V - V_c)^3 = 0^3$$

$$(a-b)^3 = a^3 - b^3 - 3ab(a-b)$$

$$V^3 - V_c^3 - 3VV_c(V - V_c) = 0$$

$$V^3 - V_c^3 - 3V^2V_c + 3VV_c^2 = 0$$

Rearrange the eq<sup>n</sup>. —

$$V^3 - (3V_c)V^2 + (3V_c^2)V - V_c^3 = 0 \quad \text{--- (6)}$$

On comparing eq (4) & eq (6).

$$3V_c = b + \frac{RT_c}{P_c}, \quad 3V_c^2 = \frac{a}{P_c} \quad \text{and} \quad V_c^3 = \frac{ab}{P_c}$$

Now,

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \cdot \frac{P_c}{a}$$

$$\text{So, } \boxed{V_c = 3b} \quad \text{--- (7)}$$

Now, from the relation,  $3V_c^2 = \frac{a}{P_c}$

$$3(3b)^2 = \frac{a}{P_c}$$

$$\therefore \boxed{P_c = \frac{a}{27b^2}} \quad \text{--- (8)}$$

$$\text{As, } 3V_c = b + \frac{RT_c}{P_c}$$

$$3 \cdot 3b = b + \frac{RT_c}{P_c} \cdot 27b^2 \quad \left[ \because \text{from (7) \& (8)} \right]$$

$$\frac{RT_c}{a} \cdot 27b^2 = 9b$$

$$\therefore \boxed{T_c = \frac{8a}{27Rb}} \quad \text{--- (9)}$$

Q.36.

The rate constant for the II<sup>nd</sup> order decomposition of  $N_2O$  follow the eqn.  $K = 5.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \cdot e^{-2900/T}$ , Determine the activation energy.

Sol.

Given that -

$$K = 5.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \cdot e^{-2900/T} \text{ ——— ①}$$

comparing with Arrhenius eqn -

$$K = A \cdot e^{-E_a/RT}$$

$E_a$  = activation energy

$R$  = gas cont.

$T$  = temp.

$A$  = freq. factor.

$$\therefore \boxed{A = 5.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}}$$

$$e^{-2900/T} = e^{-E_a/RT}$$

$$-\frac{2900}{T} = -\frac{E_a}{RT}$$

$$\frac{E_a}{R} = 2900.$$

$$\text{If, } E_a = 2900 \times R.$$

$$\text{If, } E_a = 2900 \times 8.314$$

$$\boxed{E_a = 2.4 \times 10^4 \text{ joule/mol.}}$$

$$\text{If, } E_a = 2900 \times 1.98$$

$$\boxed{E_a = \text{cal/mol.}}$$

**37. Example 12.** A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete ?

**Solution.** (i) For the first order reaction

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

when  $x = \frac{40}{100} a = 0.4 a,$

$$t = 50 \text{ minutes (Given)}$$

$$\therefore k = \frac{2.303}{50} \log \frac{a}{a-0.4a}$$

$$= \frac{2.303}{50} \log \frac{1}{0.6}$$

or  $k = 0.010216 \text{ min}^{-1}.$

(ii)  $t = ?,$

when  $x = 0.8 a$

$$k = 0.010216 \text{ min}^{-1}. \text{ (Calculated above)}$$

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

$$= \frac{2.303}{0.010216} \log \frac{a}{a-0.8a}$$

$$= \frac{2.303}{0.010216} \log \frac{1}{0.2}$$

$$= 157.58 \text{ min.}$$

- 38. Example 11.** RMS velocity of hydrogen at STP is  $1.85 \times 10^5 \text{ cm sec}^{-1}$  and its mean free path is  $1.75 \times 10^{-5} \text{ cm}$ . Calculate the collision number.

**Solution.** RMS velocity,  $\mu = 1.85 \times 10^5 \text{ cm sec}^{-1}$

$$\begin{aligned}\text{Average velocity } \bar{c} &= 0.9213 \times \text{RMS Velocity} \\ &= 0.9213 \times 1.85 \times 10^5 \text{ cm sec}^{-1}\end{aligned}$$

$$\text{Mean free path} = \frac{\text{Average velocity}}{\text{Collision number}}$$

$$1.75 \times 10^{-5} = \frac{0.9213 \times 1.85 \times 10^5}{\text{Collision number}}$$

$$\text{or Collision number} = \frac{0.9213 \times 1.85 \times 10^5}{1.75 \times 10^{-5}} = 9.734 \times 10^9 \text{ sec}^{-1}.$$

- 39. Example 12.** At  $0^\circ\text{C}$  and 1 atmosphere pressure, molecular diameter of a gas is  $4 \times 10^{-8} \text{ cm}$ . Calculate the mean free path of its molecule.

**Solution.** Mean free path is given by the equation

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \rho}$$

where  $\sigma$  is molecular diameter.

22400 ml of a gas at  $0^\circ\text{C}$  and 1 atm. pressure contains  $6.02 \times 10^{23}$  molecules.

Hence, number of molecules per c.c,

$$\rho = \frac{6.02 \times 10^{23}}{22400} = 2.689 \times 10^{19}.$$

Substituting the values in the above equation

$$\lambda = \frac{1}{1.414 \times 3.14 (4 \times 10^{-8})^2 \times 2.689 \times 10^{19}} = 0.524 \times 10^{-5} \text{ cm}.$$

- 40. Example 2.** Calculate the root mean square velocity, average velocity and most probable velocity of sulphur dioxide molecules at 427°C.

**Solution.** (a) Calculation of root mean square velocity

$$u = \sqrt{\frac{3RT}{M}}$$

Here,  $T = 427^\circ\text{C} = 427 + 273 \text{ K} = 700 \text{ K}$

$M = \text{Mol. wt. of SO}_2 = 32 + 32 = 64$

$R = 8.314 \times 10^7 \text{ ergs/degree/mol}$  (C.G.S. Units)

Putting the values in the above equation, we get

$$\begin{aligned} u &= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 700}{64}} \\ &= \sqrt{\frac{3 \times 8.314 \times 10^8 \times 70}{64}} \\ &= \sqrt{\frac{3 \times 8.314 \times 70}{64}} \times 10^4 = 5.224 \times 10^4 \text{ cm s}^{-1} \\ &= \mathbf{52240 \text{ cm s}^{-1}} \end{aligned}$$

(b) Calculation of average velocity ( $\vartheta$ )

$$\vartheta = 0.9213 \times u = 0.9213 \times 5.2240 = \mathbf{48128 \text{ cm s}^{-1}}$$