

*Biyani's Think Tank*

Concept based notes

# **Physical Chemistry**

B.Sc. Part-I (Paper-III)

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## Preface

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I am glad to present this book, especially designed to serve the needs of the students. The book has been written keeping in mind the general weakness in understanding the fundamental concepts of the topics. The book is self-explanatory and adopts the “Teach Yourself” style. It is based on question-answer pattern. The language of book is quite easy and understandable based on scientific approach.

Any further improvement in the contents of the book by making corrections, omission and inclusion is keen to be achieved based on suggestions from the readers for which the author shall be obliged.

I acknowledge special thanks to Mr. Rajeev Biyani, *Chairman* & Dr. Sanjay Biyani, *Director (Acad.)* Biyani Group of Colleges, who are the backbones and main concept provider and also have been constant source of motivation throughout this Endeavour. They played an active role in coordinating the various stages of this Endeavour and spearheaded the publishing work.

I look forward to receiving valuable suggestions from professors of various educational institutions, other faculty members and students for improvement of the quality of the book. The reader may feel free to send in their comments and suggestions to the under mentioned address.

**Author**

# Syllabus

B.Sc. Part-I : Paper-III

Physical Chemistry

## Unit-1

### 1. Mathematical Concepts and Computers

(A) **Mathematical Concepts**-Logarithmic relations curve sketching linear graphs and calculation of slopes, differentiation of functions like  $Kx$ ,  $e^x$ ,  $x^n$ ,  $\sin x$  and  $\log x$ ; maxima and minima, partial differentiation and reciprocity relations, integration of some useful/relevant functions; permutations and combinations, Factorials, Probability.

(B) **Computers**- General introduction to computers, different components of a computer, hardware and software, input-output devices; binary numbers and arithmetic, introduction to computer languages. Programming operating systems.

## Unit-II

2. **Gaseous States**- 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 isotherms 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: Root mean square, average and most probable velocities. Qualitative discussion of the Maxwell's distribution of molecular velocities, collision number, mean free path and collision diameter, Liquification of gases (based on Joule-Thomson effect).

## Unit-III

3. **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 cholestric phases.

#### **Unit-IV**

**4. Solid State-** Definition of space lattice, unit cell.

Laws of crystallography-(i) Law of constancy of interfacial angles (ii) Laws of rationality of indices (iii) Law of symmetry, Symmetry elements in crystals.

X-ray diffraction crystals. Derivation of Bragg's equation Determination of crystal structure of NaCl, and CsCl (Laue's method and powder method).

#### **Unit-V**

**5. Colloidal State-** Definition of colloids, classification of colloids. Solids in liquids (sols): properties- kinetic, optical and electrical, stability of colloids. Protective action. Hardy-Schulze law, gold number.

Liquids in solids (gels): classification, preparation and properties, inhibition, general application of colloids. Liquids in liquids (emulsions): type of emulsions, preparation. Emulsifier.

#### **Unit-VI**

**6. Chemical Kinetics-** Chemical kinetics and its scope, rate of a reaction, factors influencing the rate of a reaction Concentration, dependence of rates, mathematical characteristics of simple chemical reactions.

Zero order, first order, second order pseudo order, half life and mean life. Determination of the order of reaction-differential method. Method of integration, method of half life period and isolation method.

Radioactive decay as a first order phenomenon.

Experimental methods of chemical kinetics: conductometric, potentiometric, optical methods, polarimetry and spectrophotometry. 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 aspects.

## PHYSICAL CHEMISTRY

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**Q.1. Evaluate the followings:-**

**(i)  $\log_3 243$**

**Sol.** Let  $\log_3 243 = x$   
 $3^x = 243$   
 $3^x = 3^5$   
 $x = 5$

$\therefore \log_3 243 = 5$

**(ii)  $\log_7 343$**

Let  $\log_7 343 = x$   
 $7^x = 343$   
 $7^x = 7^3$   
 $x = 3$

$\log_7 343 = 3$

**(iii)  $\log_{10} 10,000$**

Let  $\log_{10} 10,000 = x$   
 $10^x = 10000$   
 $10^x = 10^4$   
 $x = 4$

$\log_{10} 10,000 = 4$

(iv)  $\log_{27} 9$

$$\begin{aligned}\text{Let } \log_{27} 9 &= x \\ 27^x &= 9 \\ (3^3)^x &= 3^2 \\ 3^{3x} &= 3^2 \\ 3x &= 2 \\ x &= 2/3 \\ \log_{27} 9 &= \frac{2}{3}\end{aligned}$$

Q.2. Evaluate:

(i)  $\frac{\log 32}{\log 4}$

$$\text{Sol. } \frac{\log 32}{\log 4} = \frac{\log 2^5}{\log 2^2} = \frac{5 \log 2}{2 \log 2} = \frac{5}{2}$$

(ii)  $\frac{\log 27}{\log 9}$

$$\text{Sol. } \frac{\log 27}{\log 9} = \frac{\log 3^3}{\log 3^2} = \frac{3 \log 3}{2 \log 3} = \frac{3}{2}$$

Q.3 Prove that

$$\begin{aligned}\log (1 + 2 + 3) &= \log 1 + \log 2 + \log 3 \\ \log (1 \times 2 \times 3) &= \log 6 \\ &= \log (1 \times 2 \times 3) \\ &= \log 1 + \log 2 + \log 3\end{aligned}$$

**Q.4** If  $\log (M+n) = \log M + \log n$ , show that

$$M = \frac{n}{(n-1)}$$

**Sol.**  $\log (M + n) = \log m + \log n$

$$\log (M + n) = \log Mn$$

$$M + n = mn$$

$$n = mn - m$$

$$n = M(n-1)$$

$$\boxed{M = \frac{n}{n-1}}$$

**Q.5** Find the derivative of  $(x^3 + e^x + 3^x + \cot x)$  with respect to  $x$ .

$$\begin{aligned} \frac{d}{dx} (x^3 + e^x + 3^x + \cot x) &= \frac{d}{dx} x^3 + \frac{d}{dx} e^x + \frac{d}{dx} 3^x + \frac{d}{dx} \cot x \\ &= 3x^2 + e^x + 3^x \log 3 - \operatorname{cosec}^2 x \end{aligned}$$

**Q.6** Differentiate  $x^2 \cdot \tan x - x \log x$  w.r.t.  $x$

$$\begin{aligned} &\frac{d}{dx} (x^2 \tan x - x \log x) \\ &= \left( x^2 \frac{d}{dx} \tan x + \tan x \frac{dx^2}{dx} \right) - \left( x \frac{d}{dx} \log x + \log x \frac{d}{dx} (x) \right) \\ &= (x^2 \sec^2 x + 2x \tan x) - \left( x \cdot \frac{1}{x} + \log x \cdot 1 \right) \\ &= x^2 \sec^2 x + 2x \tan x - 1 - \log x \end{aligned}$$



**Q.7** A bag contains 9 black and 12 white balls. One ball is drawn at random. What is the probability that the ball drawn is black?

**Sol.** Total Number of balls =  $(9+12) = 21$

Thus, if S is the Sample space, then  $n(s) = 21$

And, if E is the event of getting a black ball, then

$$n(E) = 9$$

$$\therefore P(\text{getting a black ball}) = \frac{n[E]}{n[S]} = \frac{9}{21} = \frac{3}{7}$$

**Q.8** Evaluate

(i)  $P_{(12,4)}$

**Sol.**

$$\begin{aligned} P_{(12,4)} &= \frac{12!}{(12-4)!} = \frac{12!}{8!} \\ &= \frac{12 \times 11 \times 10 \times 9 \times 8!}{8!} \\ &= 11,880 \end{aligned}$$

(ii)  $P_{(75,2)}$

**Sol.**

$$\begin{aligned} &= \frac{75!}{(75-2)!} \\ &= \frac{75!}{73!} \\ &= \frac{75 \times 74 \times 73!}{73!} \\ &= 5,550 \end{aligned}$$

(iii)  $P_{(8,8)}$

**Sol.**

$$= \frac{8!}{(8-8)!}$$

$$\begin{aligned}
 &= 8 ! \\
 &= 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1 \\
 &= 40,320
 \end{aligned}$$

**Q.9 In how many ways can 10 books be arranged on a shelf so that a particular pair of books shall be**

**(i) always together**

**(ii) never together**

**Sol.** (i) Since a particular pair of books can be arranged on the shelf in  $P_{(10,10)} = 10 !$  ways then we shall have to arrange 1 books on the shelf this can be done in  $P_{(9,9)} = 9 !$  ways.

Now in each of these arrangements, the two books comprising the particular pair can be arranged among themselves in  $2 !$  i.e. 2 ways.

Required Number of ways =  $2 \times 9 !$

(ii) We know that 10 books can be arranged on the shelf in  $P_{(10,10)} = 10!$  ways. Also the Number of ways of arranging 10 books so that a particular pair is never together.

$$\begin{aligned}
 &= (10 ! - 2 \times 9 !) \\
 &= (10 \times 9 ! - 2(9)!) = 8 \times 9 !
 \end{aligned}$$

**Q.10 How many 4-letter words, with or without meaning can be formed out of the letter of word "LOGARITHMS" if repetition of letters is not allowed.**

**Sol.** The word "LOGARITHMS" contains 10 different letters.

$\therefore$  The Number of required words = Number of arrangements of 10 letter, taken 4 at a time.

$$\begin{aligned}
 P_{(10,4)} &= \frac{10!}{10.4!} \\
 &= \frac{10!}{6!} = 10 \times 9 \times 8 \times 7 \times 6
 \end{aligned}$$

**Q.11** How many words with or without meaning can be formed by using all the letters of word "DELHI" using each letter exactly once?

**Sol.** The word "DELHI" contains 5 different letters

∴ The number of required words = No. of arrangement of 5 letter taken all to a

$$P_{(5,5)} = 5! = 5 \times 4 \times 3 \times 2 \times 1 = 120$$

**Q.12** Find the derivatives of:-

(i)  $X^9$

**Sol.**  $\frac{d}{dx} (x^n) = nx^{n-1}$

$$\begin{aligned} \frac{d}{dx} (x^9) &= 9x^{9-1} \\ &= 9x^8 \end{aligned}$$

(ii)  $x^{-5}$

**Sol.**  $\frac{d}{dx} (x^{-5}) = -5x^{-5-1}$

$$\begin{aligned} &= -5x^{-6} \\ &= \frac{-5}{x^6} \end{aligned}$$

**Q.13** What is Software?

**Ans.** Software is a sequence of instructions written in computer language to perform a specific job such as drafting letters and reports.

**Q.14** Write short note on relationship between Hardware and Software.

**Ans.** There is a special relationship between hardware and software. Both are complementary to each other. Nothing useful can be done with the

computer hardware on its own and software cannot be utilized without supporting hardware.

A cassette player and the cassettes are hardware while songs recorded on the cassettes are its software. To get a particular job done by a computer, the relevant software should be loaded in the hardware before processing starts.

**Q.15 Write short notes on:-**

**(i) Printers**

**(ii) Keyboard**

**(iii) Mouse**

**Ans. (i) Printers:** Printers are the commonly used primary output devices to prepare permanent documents in human readable form (hard copy). There are several types of printers that are designed for different types of application. Depending on their speed and approach of printing, printers are classified as character printers, line printers and page printers.

**(ii) Keyboard:** Programs and data are entered into a computer through a keyboard which is attached to a micro-computer or the terminal of a mini or large computer. Data is entered into the computer by pressing a set of keys available with these devices.

**(iii) Mouse:** A Mouse is a pointing device. It is held in one hand and moved across a flat surface it is used to draw sketches, diagrams etc. on the computer screen it is also used to edit text.

**Q.16 Add the binary numbers 101 and 10 in both decimal and binary form.**

BINARY	DECIMAL
101	5
+ 10	+ 2
<u>111</u>	<u>7</u>

**Q.17 Add the binary numbers 10011 and 1001 in both decimal and binary form.**

Ans.	BINARY	DECIMAL
Carry	11	Carry 11
	10011	19
	+ 1001	+ 9
	<u>11100</u>	<u>28</u>

**Q.18 What is Multi Programming?**

**Ans.** In case of batch processing, the batched programs are loaded one after another in sequence into the main memory for processing. Once loaded, a program will remain in the main memory until its execution is completed thus, the program which is currently being executed will be the sole occupant of the users area of the main memory and it will have the CPU exclusively available to itself. When there is only one program in main memory, two of the systems most powerful resources may be under-utilized, its expensive memory and full capabilities of the CPU.

In order to overcome the problem of under-utilization of main memory and the CPU, the concept of multi programming was introduced in operating system. "Multiprogramming is the name given to the interleaved execution of two or more different and independent programs by the same computer." With the storage-resident supervisor concept we have been introduced to the motion of having two programs in the main memory at the same time: the supervisor for overall system control and the user program for performing user's task. In multiprogramming, this concept is carried one step further by placing two or more user's programs in main memory and executing them co-currently the CPU switches from one program to another almost instantaneously since the operating speed of CPU is much faster than that of I/O operations, the CPU can allocate time to several progress instead of remaining idle when on is busy with I/O operations. In multiprogramming system, when one program is waiting for I/O transfer, there is another program ready to utilize the CPU, thus it is possible for several user to share the time of the CPU.

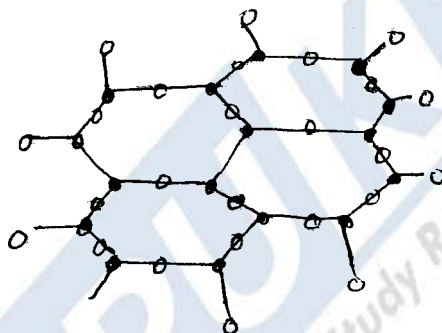
**Q.19** Write short notes on types of crystals. What is the difference between crystalline and amorphous solids.

**Ans.** When substance is at low temperature then intermolecular forces are not enough to hold the molecules together in more or less fixed position. The material acquires a shape and is then said to be in the solid state the so called solid material may be divided into two distinct classes:-

(i) Crystalline solids

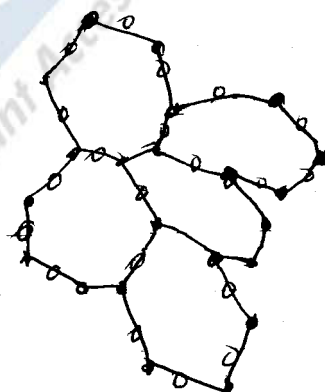
(ii) Amorphous solids

**(i) Crystalline solids:** In a crystalline solid, atoms, molecules or ions are arranged in a regular repeating three dimensional pattern and has a characteristic geometrical shape. Sugar and Salt are crystalline solids.



**Fig. Crystalline solids**

**(ii) Amorphous solid:** In amorphous solids, the atoms, molecules or ions are arranged in a random manner and lacks an ordered crystalline lattice. Rubber, plastic and glass are the example of amorphous solids.



**Fig. Amorphous solid**

In their disordered structure, amorphous solids resemble liquids thus glasses are regarded as Super-cooled or Highly viscous liquid.

In very old window panes, glass become slightly thicker at the bottom due to gradual downward flow.

**Difference between Crystalline and Amorphous Solids :**

- (i) In crystalline solids, the constituent particles are arranged in a regular fashion containing short range as well as long range orders while in amorphous solids, the constituent particles are not arranged in any regular fashion, there may be at the most some short range orders only.
- (ii) Crystalline solids have sharp M.P. while amorphous solids melts overcome range of temperature.
- (iii) The properties of crystalline solids like electrical conductivity, thermal expansions, refractive index has different values in different directions. While properties of amorphous solids has same value in different directions.
- (iv) Crystalline solids undergo a regular cut while amorphous solids undergo a ir-regular cut.

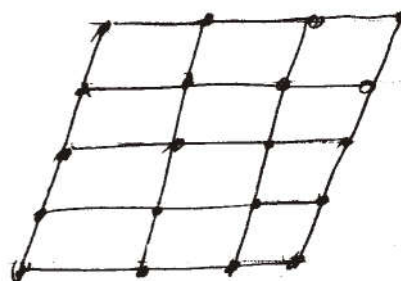
**Q.20 What do you mean by space lattice and unit cell?**

**Ans.** The Particles (atoms, molecules or ions) in crystal are arranged in regular patterns that extent in all directions the overall arrangement of particles in a crystal is called crystal lattice, space lattice or simple lattice.

The simple basic unit or the building block of the crystal lattice is called the unit cell.



Unit cell



Lattice



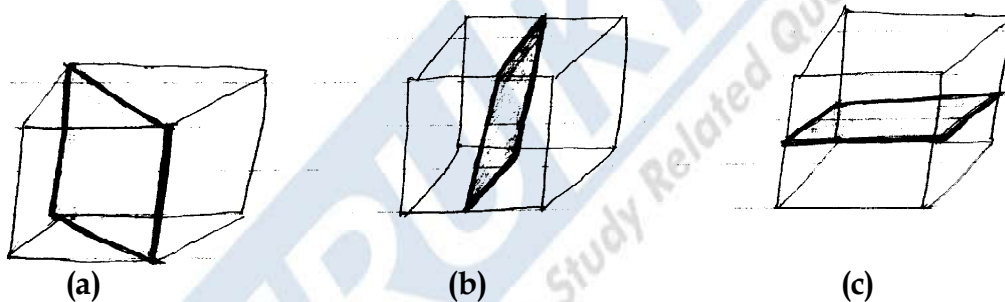
**Q.21 Explain the symmetry elements with suitable examples.**

**Ans.** A symmetry element is a geometrical entity such as a line (or axis), a plane or a point with respect to which one or more symmetry operations may be carried out.

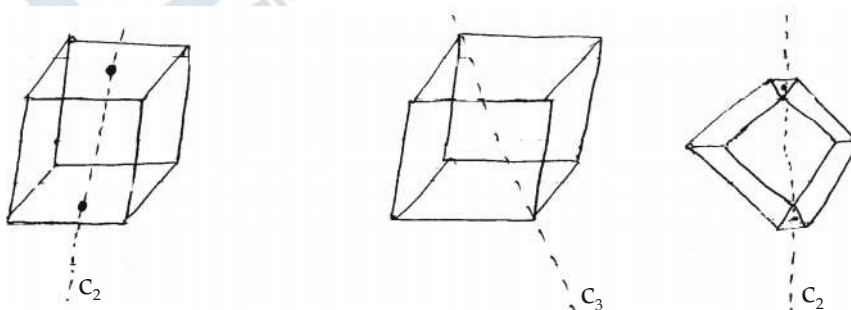
Symmetry elements are of following types:

- (a) Plane of symmetry
- (b) Axis of symmetry
- (c) Centre of symmetry

**(a) Plane of Symmetry:** When an imaginary plane passes through the centre of crystal and divide it into two equal parts which are mirror image of each other then a crystal is said to possess a plane of symmetry.



**(b) Axis of Symmetry:** It is a line about which the crystal may be rotated so that it represents the same appearance more than once during a complete revolution. If the equivalent configurations occurs twice, thrice, four and six times, i.e. after rotation of  $180^\circ$ ,  $120^\circ$ ,  $90^\circ$  and  $60^\circ$ , the axis of rotation are known as two fold (diad), three fold (trid), four fold (tetrad) and six fold (hexad), axis of symmetry respectively the axis of symmetry represented by C.





(c) **Centre of Symmetry:** It is a point that any line drawn through will meet the surface of the crystal at equal distances on either side. A crystal may have a number of planes or axis of symmetry but it can only have one centre of symmetry. A cube has 13 axis of symmetry (three three fold four four fold and six two fold). 9 planes of symmetry and one centre of symmetry i.e. 23 elements of symmetry altogether.

**Q.22 What do you mean by crystallography. Explain the three law of crystallography.**

**Ans.** Crystallography is the science of crystals which is denoted to the study of their development and growth, their external form, internal structure and physical properties.

- (a) Steno's law
- (b) Law of Constancy of symmetry
- (c) Law of rationality of intercepts.

**(a) Steno's Law**

According to this law "the crystal of same substance can have different shapes depending upon the numbers and size of faces but the angles between the corresponding faces remains constant.



**(b) Law of Constancy of symmetry:** According to this law "All crystals of the same substance have the same elements of symmetry.

**(c) Law of rationality of intercepts:** The law of rationality of intercepts or indices proposed in 1874 by Havy states that

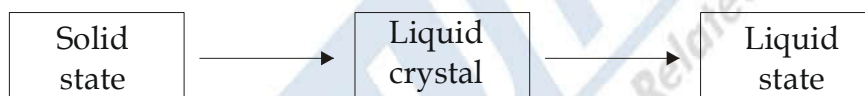
It is possible to choose along the three co-ordinate axes unit distance (a, b, c) not necessarily of the same length, such that the ratio of the three intercepts of any plane in the crystal is given by  $Ma : nb : Pc$  where m, n and P are either integral whole numbers including infinity or fractions of whole numbers.

**Q.23 Briefly discuss the structure of liquid state.**

**Ans.** Liquid is a material which takes the shape of the container in which it is taken. It's not necessary like gas that it unit completely fill the container. Liquid may be regarded as "condensed gas" or "Molten Solids". In liquids, molecules are not rigidly fixed they have some freedom of motion that's why liquid has definite volume but not a definite shape.

**Q.24 What do you mean by liquid crystals?**

**Ans.** When a solid melts, the vibrations of its constituent particles acquire such magnitude that they lapse into translatory motions and a cloudy liquid state is form the term liquid crystals is made up of liquid and crystals the word liquid is there because these tend to take the shape of the container and the word crystals is then because they still contain one or more dimensional arrays.

**Q.25 What are the types of liquid crystals? Discuss each in brief.**

**Ans.** Liquid crystals have been classified into following types-

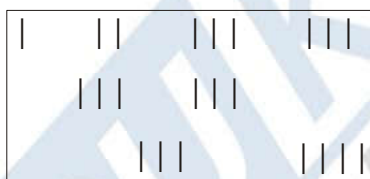
- (i) Nematic crystals
- (ii) Cholesteric crystals
- (iii) Smectic crystals

**(i) Nematic crystals:** Thread like liquid crystals are called as Nematic liquid crystals this word is derived from Greece word "Nematos" meaning thread. In nematic liquid crystals, the molecules are aggregated together in groups with their axis parallel to one another. These molecules move sideways or up and down along their length. Each molecule can rotate around its axis. In an electric or magnetic field, the groups of Nematic liquid crystals get oriented in the same direction.



**(ii) Cholesteric Crystals:** Those liquid crystals which have some nematic characters and some smectic characters are called as Cholesteric liquid crystals. These phases/crystals show strong colour effects in polarized light which shows its layer structure. But it has much thicker layers than smectic liquid crystals.

**(iii) Smectic Liquid Crystals:** Soap like liquid crystals are called as Smectic liquid crystals. This word is derived from Greece word for soap. In smectic liquid crystals, molecular are arranged in layer form and show periodicity to a certain extends.



**Q.26 Discuss in short the theory of liquid crystals.**

**Ans.** Liquid crystals can be explain by Swarm theory. This theory was proposed by Bose. According to this theory constituent molecules are arranged parallally in different groups, called Swarm, but there is no definite arrangement of these groups. Every Swarm is like a small crystal but they are randomly scattered in the whole of the mass. Because of these swarm, light get scattered and causes turbidity. As temperature of liquid crystals increases swarms get very small and scattering of light get stop. As a result liquid crystals become transparent and converts into clear liquid.

**Q.27 What are Colloids?**

**Ans.** Those substances which can diffuse very slowly in solution and cannot pass through animal or vegetable membranes are called as "Colloids". For e.g. starch, gelatin, silicic acid, proteins etc.

This class of substances generally exist in amorphous or gelatinous condition hence the name colloids meaning "glue form".

**Q.28 Give the basis of classification of Colloids.**

**Ans.** There are number of basis for the classification of colloids.

- (1) Depending upon the nature of the dispersed phase that of dispersion medium.
- (2) Depending upon the appearance of colloids.
- (3) Depending upon the interaction of the two phases.
- (4) Depending upon the electrical charge on the dispersed phase.
- (5) Depending on the structure of colloids particles.
- (6) Based on particle shape.
- (7) Based on chemical composition.

**Q.29 What are Sols? Describe the optical properties of it.**

**Ans.** When a colloidal solution appear as fluid, it is termed as Sols. Sols are named after dispersion medium. For example, when dispersion medium is water, they are called as "hydrosols" when the dispersic medium is alcohol they are called as alcohols and so on.

Dispersed phase + Dispersion medium = Dispersion system (Colloidal Solutions)

Solid + Liquid = Sol

Colloidal Sols show the following optical properties-

- (1) Optical rotation by solution of high polymers.
- (2) Optical anisotropy in colloids.
- (3) Tyndall effect.

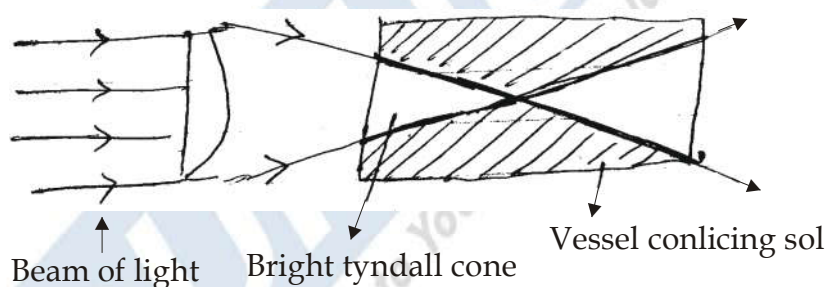
**(1) Optical rotation by solution of high Polymers:** Molecules of some organic colloids are optically active. Hence they rotate the plane of polarised light either towards left or right.

(2) **Viscosity of Sols:** Viscosity is a tendency of fluid to resist flow it is directly related to the shape of particles therefore viscosity dependence on concentration, temperature etc as concentration and temperature increases viscosity also increases viz sols flow more easily.

(3) **Tyndall effect:** If a homogeneous solution is observed in the direction of light, it appears clear.

If a homogeneous solution is observed from a direction at right angles to the direction of light, it appears perfectly dark.

But when a powerful beam of light is passed through a colloidal solution (in place of Homogeneous solution) placed in a darkened room, the sol appears to be luminescent when we view from direction at right angles to the direction of light because it get scattered and the maximum scattered intensity being in the plane at right angles to the path of light the path beam becomes visible. The effect was first observed by Faraday and later studied in detail by Tyndall and hence is called as "Tyndall Effect".



### Q.30 Describe the electrical properties of Sols?

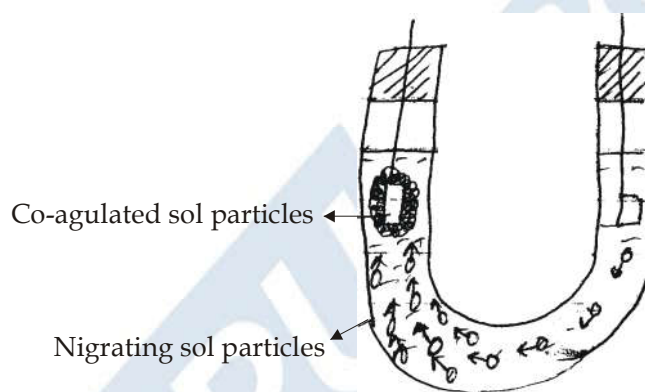
**Ans.** Sol colloids particles carry an electric charge. When sols are placed in the electric field they show 4 type of effect. Such effects are termed as "Electro-Kinetic effects.

These electro-kinetic effects are as follows:-

- (i) Electrophoresis or cataphoresis.
- (ii) Electro osmosis or Electro endosmosis

**(1) Electrophoresis or Cataphoresis:** All Colloidal particles carry an electric charge on them this can be easily demonstrated by placing the colloidal particles in an electric field. For this purpose colloidal solution is taken in a U-tube and the two platinum electrodes are dipped in sol. The current is then switched on closing the circuit it is found that colloid particles move to the oppositely charged electrode and on reaching that electrode they get discharged. As soon as the charge of the particles is neutralised particles settle down at the bottom. This movement of the colloid particles under the influence of electric field is k/a.

#### Cataphoresis or Electrophoresis



Cataphoresis has many important applications e.g.

- (1) Determining the charge on the colloidal particles Direction of movement of the colloidal particles in the electric field shows the charge on them.
- (2) It can also be used to determine the rate at which colloidal particles migrate under the influence of an electric field.
- (3) It is also used in the identification & determination of homogeneity.

#### Q.31 Write a Short Note on "Hardy-Schulze Law".

**Ans.** The colloidal sols are stable by the presence electric charges on the colloidal particles.

- Because of the electric repulsion the particles do not come close to one another.



- As charge removes by any means, particles get aggregate and hence precipitation occurs.
- The process by means of which the particles of the dispersed phase in a sol are precipitated is known as "Coagulation or flocculation".
- A common method of producing precipitation is by the addition of electrolytes.

This phenomenon was studied in detail by Schulze, Linder, Picton and Hardy and their observations have been summarized in the form of Hardy-Schulze laws given as below:

- (a) The ion which brings co-agulation (aggregation) of a colloidal solution has opposite sign to that on the colloidal particle. Hence for coagulation of (+)vely charged  $\text{Fe}(\text{OH})_3$  solution anion is required which is associated with it.
- (b) A certain amount of electrolyte is necessary for co-agulation this amount varies, with the valency of the effective ion. Thus much more quantity of univalent cation is required than bi-valent ion similarly bivalent ion are much more required than the trivalent ion.

Thus the precipitation value or co-agulation value is defined as the minimum concentration of the electrolyte required to precipitate a given solution.

There are two possibility of co-agulation:

- (i) If two oppositely charged colloids are mixed then they will come close together and get aggregate that's why precipitation occurs. This type of co-agulation is known as Mutual co-agulation.
- (ii) If two oppositely charged colloids (Particles) are mixed together and they don't have equal charges the only partial co-agulation will take place.

**Q.32 Discuss the stability of Colloids.**

**Ans.** In Colloids, Particles has electric charges of same sign. Due to electrostatic attraction such lyophobic sols are stable. But for the stability of hydrophilic sols two factors are responsible.

(i) its charge

(ii) its hydration

- Its particles are heavily hydrated and water envelopes surrounding the particles.

So for co-agulation of this hydrophilic sols removal of charge is must. Secondly removal of water layers is also necessary for this purpose, we add dehydrating agent like alcohol or acetone.

**Q.33 Explain the Protection action of Colloids.**

**Ans. Protection:** When certain hydrophilic colloids are added to a hydrophobic colloid then stability of hydrophobic colloids get increase. Now addition of small electrolyte is not able to precipitate the hydrophobic colloids. This action of hydrophilic colloids to prevent precipitation of hydrophobic colloid by the electrolytes is called as Protection and the hydrophilic colloid is called Protective Colloid.

- Latter protective colloids (hydrophilic colloids can be evaporated to dryners and when dry mass is treated with water it redissolves to give the colloidal solution. Thus protective colloid converts an irreversible (Hydrophobic) colloid into a reversible colloid.

**Explanation:-**

- The particles of the protected colloid get adsorbed. On the particle of the hydrophobic colloid, and form a protective layer around it.
- The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.
- The increase in stability of the hydrophobic and colloid is due to the mutual adsorption of the hydrophilic and hydrophobic colloids.
- The smaller particles whether of the protective colloid or of the hydrophobic colloid are adsorbed on the bigger particles.

**Q.34 What do you understand by GOLD NUMBER.**

**Ans.** The power of the hydrophilic colloid to prevent the precipitation of a lyophobic colloid by addition of an electrolyte depends upon the nature



of the substance this protective nature of various hydrophilic substances can be expressed by gold Number.

According to Zsigmondy, the gold number may be defined as -

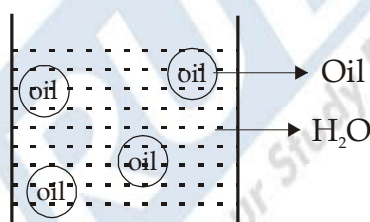
The Number of milligrams of Protective colloid which just prevents the coagulation of 10 ml of a given gold sol by the addition of 1 ml of 10% Sodium chloride to it.

Smaller the gold Number, higher the protective power of a colloid.

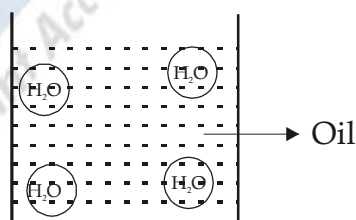
**Q.35 What is an emulsion? Describe the main types of emulsions. How are emulsions prepared? Give any two uses of emulsion.**

**Ans.** Emulsion is a colloidal system consisting of immiscible liquids. Emulsions are classified two classes:

**(1) Oil in Water (O/W) type:** In these emulsions oil forms the dispersed phase and water, the dispersion medium. For e.g. milk, vanishing cream etc. these are also called aqueous emulsions.



**(2) Water in Oil (W/O) Type:** In these emulsions water is in the dispersed phase and oil in the dispersion medium. For example butter, cold cream etc. are called oil emulsions.



**Preparation of emulsions:**

- Emulsions are obtained by spraying mixture of phases through narrow nozzles.

- Type of obtained emulsion depends on the nature of the emulsifying agent used.
- According to Bancroft rule the phase in which the stabilizer is more soluble becomes the external phase.
- Neutral soaps which are insoluble in hydrocarbons but soluble in water give oil-in-water emulsions while acid soaps which are more soluble in hydrocarbons give water-in-oil emulsions.
- Emulsions can also be prepared by using ultrasonic waves.
- Emulsion is also possible with stabilizers insoluble in both phases. In these cases the phase which wets the emulsifier better becomes the outer phase.
- Clay, glass powder, calcium carbonate, pyrites, are easily wetted by water so aqueous emulsions are easily form in their presence utile lamp black or soot which is more easily wetted by an oil gives oily emulsions.

#### Uses of Emulsions:

**(1) Medicine:** Numerous medicines are emulsions. In such forms they have been found to be more effective cod liver oil and castor oil used as medicines are emulsions. Soaps and detergents has the properties of emulsification and so they are used for washing clothes and utensils.

**(2) Articles of daily use:** Milk, which has all the qualities of complete food is an emulsion of fat dispersed in water is stabilized by Casein. Cream is an emulsion of the oil-water type. Butter is also emulsion of water-oil type.

**(3) Cosmetics:** Both types of emulsion (O/w type and W/O type) are used in pharmacy and cosmetics. Lotions, creams and ointments are emulsions stabilised by lanoline.

**(4) Industry:** Emulsions of oils and fats are used in leather industry for making leather soft. Asphalt emulsified in water is used for building roads, without the necessity of melting the Asphalt. The Latex obtained from the sap of certain trees is an emulsion of negatively charged rubber particles dispersed in water.

**Q.36 Write a Short Note on "Emulsifiers".**

**Ans.** In order to prepare stable emulsions it is important to add a third component known as emulsifier or emulsifying agent in suitable amounts.

Several types of emulsifier are known:

- (1) Long chain compounds with polar groups such as soap, sulphonic acid sulphates etc.
- (2) Most of the lyophilic colloids also act as emulsifier such as glue, gelation etc.
- (3) Certain insoluble powders as day, lamp back etc.
- (4) Soluble substances like iodine also act as emulsifier.

**Role of an Emulsifier-**

An emulsifier can act in two ways:-

- (1) It may be more soluble in one liquid than in the other.
- (2) The emulsifier may be insoluble in both the liquids but not unequally wetted by two.

**Q.37 What are gels? How are they classified? Describe various methods for the preparation of gels.**

**Ans.** A gel is a colloidal semi-solid, system rich in liquid phase. Thus a gel is having two components one is solid and other is liquid.

**Classification of gels:-**

The gels may be classified on the following basis-

- (1) On the basis of dispersion medium.
- (2) On the basis of size of particles.
- (3) On the basis of chemical composition.
- (4) On the basis of their properties.

On the basis of their mechanical properties, gels are of two types-

**(i) Elastic or Heat reversible gels:** These gels are reversible to heat. Such gels may be prepared by dissolving the substance in warm water. It is then cooled till it sets of these gels are dehydrated they convert into

the elastic solid form. The gel is again regenerated by adding water. On elastic gels of the fibrils composing the gel are flexible on hydration, these fibrils expand again to form the gel again.

**(ii) Non-elastic or irreversible type gels:** These gels may be prepared by adding water to dry solid. When dried they lose their acidity and becomes glassy. The rigidity of these gels increases with time. But in case of silicic acid gel, the volume decreases on drying, this decrease is having a particular unit, beyond which the air enters in the cavities of the gel.

#### **Methods for the Preparations of Gels:**

##### **(1) By cooling of colloidal solutions:**

- Gels of gelatine and agar-agar are obtained by cooling their sols of moderate concentrate (Neither low Nor high) in hot water.
- In doing so, the particles of the sols come closer to give a semi-solid mass enclosing the entire dispersion medium within itself. This results in a semi-rigid gel structure.

**(2) By double decomposition:** The gels of some sols can be prepared by the process of double decomposition, thus silicic acid gel can be prepared by adding water to sodium silicate. During this double decomposition, free silicic acid gets formed. Due to this acid liberation, it rapidly sets to a solid gel.

**(3) By enhance of solvents:** Some of the hydrophobic gels are prepared by this method. For example when ethyl alcohol is added rapidly to a fairly concentrated aqueous solution of calcium acetate, the salt separates out to give a colloidal solution. When allowed to stand it undergoes gelation (When a sol is cooled, it sets to a semi-solid gel).

#### **Q.38 Discuss the application of Colloids.**

**Ans.** Colloids play a very important role in everyday life as well as in industry, agriculture, medicine and biology. The following discussion will be of interest-

**(1) Smoke Screens:** Smoke screens generally consist of very fine particles of titanium oxide dispersed in air and are ejected from aeroplanes. As

titanium oxide is very heavy, the smoke screen drops down rapidly as a certain of dazzling whiteness therefore these are used in warfare for concealment and camouflage.

**(2) Formation of deltas:** The deltas at the mouth of great rivers are formed by the precipitate of the charged clay particles, carried us suspension in the river water by the action of salts present in sea water.

**(3) Artificial rain:** Clouds consist of charged particles of water dispersed in air. Rain is caused by the aggreption of these minute particles. Some workers have succeeded in causing such aggregation by artificial means such as by throwing electrified sand from aeroplanes.

**(4) Detergent action of soap:** Most of the dirt or dust sticks on to grease or some oily material which somehow gathers on cloth. As grease is not easily wetted by water, it is difficult to clean the garment by water alone. The addition of soap lowers the interfacial tension between water and grease and this causes the emulsification of grease in water. The mechanical action, such as rubbing etc. releases the dirt.

**(5) Clarification of Water:** Sometimes slight turbidity is noticed in water. This is due to presence of vegatively charged particles of very fine day. The addition of Potash alum or aluminium sulphates furnishes the trivalent aluminium ions ( $Al^{+3}$ ) which cause the coagulation of the day particles, therefore it settle down leaving water in clear state.

**(6) Sewage disposal:** Sewage water consists of particles of dirt, rubbish mud etc which are all colloidal in nature and carry an electric charge and therefore do not settle down easily. If an electric field is created

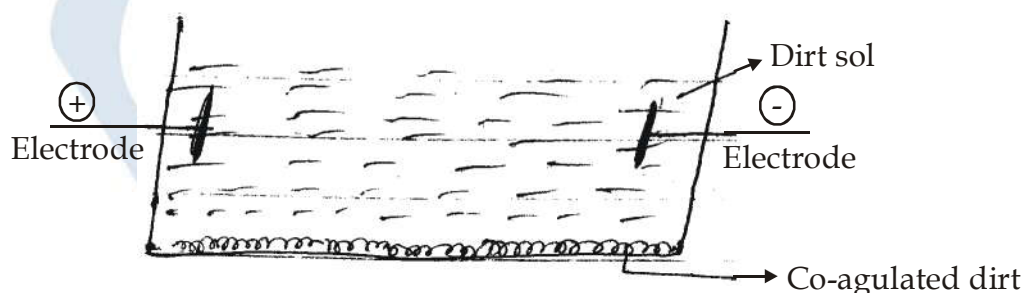


Fig. Sewage Disposal

in the sewage tank, the particles will migrate to the oppositely charged electrodes, get neutralised and settle down at the bottom. This deposit may be utilized as manure and the remaining water may be used for irrigation purposes.

**Q.39 Write the Postulates of Kinetic theory of gases.**

**Ans.** Kinetic theory of gases is also called as Microscopic Model of gases.

- It is developed by following scientists
  - (i) Kronig
  - (ii) Clausius
  - (iii) Maxwell
  - (iv) Boltzmann
- This theory was developed to explain the various gas laws or behaviour of gases such as why gases exert Pressure? Why volume is inversely proportional to the Pressure etc.
- the important assumptions of this theory are as follows:-
  - (i) A gas is made up of small particles called as Molecules.
  - (ii) These small particles behave like solid, spherical and perfectly elastic particles.
  - (iii) These particles are present far away from each other that's why they neither have attraction force nor repulsion force.
  - (iv) These molecules move in straight line in all directions rapidly collide with each other and wall as well.
  - (v) The molecules collisions are perfectly elastic (they come back to their position), i.e. there is no net loss or gain of energy after collision that's why all the molecules are still moving, they don't get stop.
  - (vi) In a gas, different-different molecules have different-different speed (velocities) and therefore different-different kinetic energy to move.
  - (vii) This kinetic energy may be transferred from one molecule to another but it cannot be convert in any other form of energy such as heat.



- (viii) Gas exerts pressure because of hits or bombardments of the molecules on the walls of the containing vessel. This force which is exerted on the per unit area of the wall is called as Pressure of gas.
- (ix) the average kinetic energy of all the molecules is directly proportional to the absolute temp. As temperature increases, velocity (speed) of Molecules increases. As a result, kinetic energy of the molecules also increases.

**Q.40 What would happen if the Molecular collisions are Non-elastic?**

**Ans.** If the collisions are non-elastic, there would be constant loss of energy. Because of which, molecular motion would be slow down and ultimately settle down at the bottom of the container like precipitate.

**Q.41 Define the law of corresponding states and obtain the reduced equation of state.**

**Ans.** All gases give same type of isotherms (Plot/curve) near critical point. (above which liquefaction doesn't occur).

- But these isotherms doesn't occur at same time since the values of 'a' and 'b' (van der waal constants) are different for different gases.
- So In 1881, Van der Waals suggested that if the Pressure, volume and temperature of a gas are expressed in terms of its critical pressure, critical volume and critical temperature then we can obtain an important generalization called the Principle of corresponding states.

Let

$$\frac{P}{P_c} = P_r \text{ or } P = P_r P_c \quad \dots(1)$$

$$\frac{V}{V_c} = V_r \text{ or } V = V_r V_c \quad \dots(2)$$

$$\frac{T}{T_c} = T_r \text{ or } T = T_r T_c \quad \dots(3)$$

where  $P_r$ ,  $V_r$  and  $T_r$  are called reduced Pressure, reduced volume and reduced temperature respectively.

On substituting the value of  $P$ ,  $V$  &  $T$  in Van der Waal equation for 1 mole of gas, as follows:

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \quad \dots(4)$$

or

$$\left( P_r P_c + \frac{a}{(V_r V_c)^2} \right) (V_r V_c - b) = RT_r T_c \quad \dots(5)$$

Since

$$P_c = \frac{a}{27b^2}, \quad V_c = 3b, \quad T_c = \frac{8a}{27Rb}$$

On substituting the value of  $P_c$ ,  $V_c$  &  $T_c$  in eqn (5) we get following eqn

$$\left( P_r \cdot \frac{a}{27b^2} + \frac{a}{V_r^2 (3b)^2} \right) (V_r \cdot 3b - b) = RT_r \cdot \frac{8a}{27Rb} \quad \dots(6)$$

...(7)

$$\left( P_r \cdot \frac{a}{27b^2} + \frac{a}{V_r^2 9b^2} \right) (V_r 3b - b) = RT_r \cdot \frac{8a}{27Rb}$$

On rearranging

...(8)



$$\left( P_r \cdot \frac{a}{27b^2} + \frac{a}{9V_r^2 b^2} \right) (3V_r b - b) = RT_r \frac{8a}{27Rb}$$

On dividing both sides by  $\frac{a}{27b}$

Or

Multiply both sides with  $\frac{27b}{a}$

$$\frac{27b}{a} \left( P_r \cdot \frac{a}{27b^2} + \frac{a}{9V_r^2 b^2} \right) (3V_r b - b) = RT_r \frac{8a}{27Rb}$$

Or

$$\left( \frac{27b}{a} \times \frac{P_r a}{27b^2} + \frac{27b}{a} \times \frac{a}{9V_r^2 b^2} \right) (3V_r b - b) = \frac{RT_r}{27Rb} \times \frac{27b}{a}$$

Or

$$\left( \frac{P_r}{b} + \frac{3}{bV_r^2} \right) (3V_r b - b) = 8T_r$$

Taking 'b' common

$$\left( P_r + \frac{3}{V_r^2} \right) \frac{1}{b} \times b (3V_r - 1) = 8T_r$$

Reduced equation of state

- This equation doesn't involve a, b or R constants, therefore this is applicable to all gases and liquids.
- This equation is also called as Reduced equation of states.

**Q.42 State the significance of "law of corresponding state".**

**Ans.** The physical significance of this equation is that if two or more substances have same reduced pressure ( $P_r$ ) and same reduced temp. ( $T_r$ ) then they will surely have the same reduced volume ( $V_r$ ).

**Q.43 Discuss root mean square velocity, average velocity and most probable velocity. Give relation between them.**

**Ans.** Molecular speeds are generally expressed in terms of

- (i) Root mean square speed
- (ii) Average velocity
- (iii) Most probable speed

**(i) Root mean square speed:** It is the square root of the mean of the square of speeds of various molecules of the gas at a given temperature.

It may be denoted by Ur.m.s. or  $\langle C^2 \rangle^{1/2}$ .

If  $V_1, V_2, V_3, \dots$  are speeds of different molecule, then

$$\langle C^2 \rangle^{1/2} = U_{\text{r.m.s.}} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \dots}{N}}$$

Or

$$\langle C^2 \rangle^{1/2} = U_{\text{r.m.s.}} = \left[ \frac{V_1^2 + V_2^2 + V_3^2 + \dots + V_n^2}{N} \right]^{1/2}$$

Alternatively if  $V_1$  is the speed of  $N_1$  Molecules,  $V_2$  is the speed of  $N_2$  Molecular and so on then

$$\langle C^2 \rangle^{1/2} = U_{\text{r.m.s.}} = \sqrt{\frac{N_1 V_1^2 + N_2 V_2^2 + N_3 V_3^2 + \dots}{N_1 + N_2 + N_3 + \dots}}$$

Root means square speed is given by the expressions -

$$U_{\text{r.m.s.}} = \sqrt{\frac{3RT}{M}} \quad \text{or} \quad \sqrt{\frac{3PV}{M}}$$

- It may be derived by using the kinetic equation of gas as follows-

$$\boxed{PV = \frac{1}{3} mnc^2} \quad \text{Kinetic gas equation} \quad \dots(1)$$

Or

$$\boxed{\frac{3PV}{mn} = c^2} \quad \dots(2)$$

Or

$$\boxed{c = \sqrt{\frac{3PV}{mn}}} \quad \dots(3)$$

Since for 1 mole gas, ideal gas eqn is

$$\boxed{PV = RT} \quad \dots(4)$$

$$\boxed{mn = M} \quad \text{Molar Mass} \quad \dots(5)$$

Putting the value of eqn (4) & (5) in eqn (3) we get

$$\boxed{c = \sqrt{\frac{3RT}{M}}}$$

### (ii) Average Velocity

- Average velocity can be represented by  $\langle C \rangle$  or  $C$
- It is an arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature.
- If  $C_1, C_2, C_3, \dots, C_n$  are the individual velocities of the gas molecules and  $n$  is their total number, then average velocity is given by

$$\boxed{\langle c \rangle = \frac{c_1 + c_2 + c_3 + c_4 + \dots + c_n}{n}}$$

- If  $C_1, C_2, C_3, \dots, C_n$  are the velocities possessed by groups of  $n_1, n_2, n_3, \dots$  molecules of the gas, respectively then, average velocity is given

by...

$$\langle c \rangle = \frac{n_1 c_1 + n_2 c_2 + n_3 c_3 + \dots}{n_1 + n_2 + n_3}$$

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

**(iii) Most Probable Velocities:**

- It may be denoted by  $C_p$  or  $\alpha$
- It is defined as the velocity possessed by maximum Number of

molecules of a gas at a given temperature.  $\alpha = \sqrt{\frac{2RT}{M}}$  M = Molecular of Mass of Gas.

**Q.44 Explain Maxwell-Boltzmann's law of distribution of Molecular velocities. Discuss the effect of temperature on the velocity distribution of molecules. Establish a relation between most probable velocity, root mean square velocity and average velocity of Molecules.**

**Ans.** As we have discussed, gas is a collection of small particles separated from the one another by large empty space and move rapidly and randomly in all the directions.

- In the course of their motion, they collide with one another and also with the walls of the container.
- Due to frequent collisions, the speeds and direction of motion of molecules keep on changing. Thus, all the molecules in a sample of a gas do not have same speeds.
- The manner in which the molecular velocities changes from almost zero to very high velocities, was for the first time worked out by J.C. Maxwell in 1860, using the theory of probability.
- The results obtained by him are expressed in the form of Law of distribution of Molecular Velocities.

- Mathematically, it can be expressed as follows-

$$\frac{1}{n} \frac{dn}{dc} = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \cdot e^{-\frac{MC^2}{2RT}} \cdot c^2$$

Here C = Velocity of Molecules

$\frac{dn}{n}$  = fraction of molecules having velocities between C and C + dc (dc represents a small variation of velocity)

Or

It represents the probability of finding the molecules possessing velocity in this very small change.

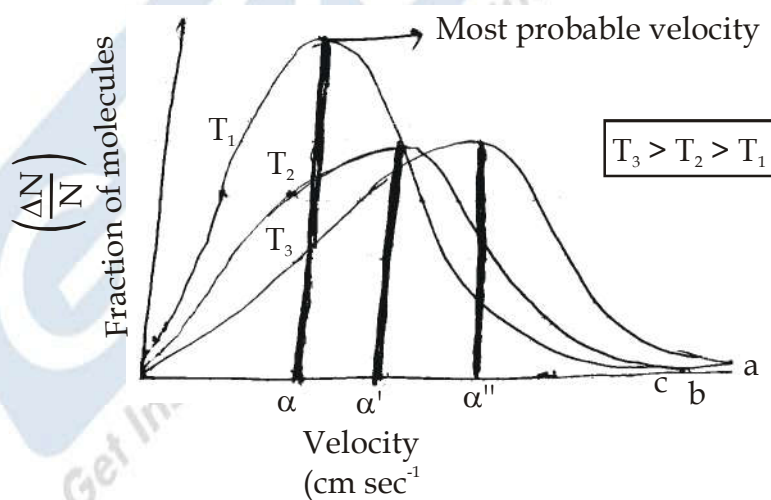
M = Molecular weight

R = Gas constant

T = absolute temp.

e = base of natural logarithm

### Graphical Representation of Maxwell Law



Thus Maxwell plotted the fraction of molecules having different speeds against the speeds at particular temperature. The curve so obtained is

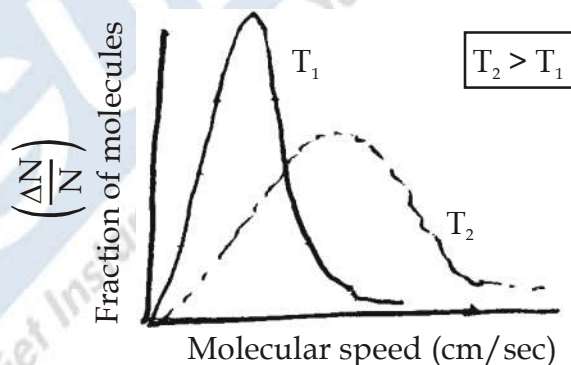
called Maxwell's distribution curve.

The important features of Maxwell's distribution curve can be summed up as follows-

- (i) The fraction of molecules with very low or very high velocities (speeds) is very small.
- (ii) The fraction of molecules possessing higher and higher speeds goes on increasing till it reaches the peak and thereafter it starts decreasing.
- (iii) The maximum fraction of molecules possess a velocity (or speed) corresponding to the peak in the curve. This speed corresponding to the peak in the curve is referred to as 'Most Probable Speed' viz speed possessed by the maximum fraction of molecules at a particular temperature.

#### Effect of temperature on distribution of Speeds

- The fraction of molecules having most probable speed remains the same so long as temperature remains same.
- On increasing the temperature of the gas, the molecular motion becomes rapid.
- Consequently, the value of most probable speed also increases.
- The entire distribution curve, shifts towards right with rise in temperature as shown below.



**Fig. Maxwell's distribution curves at different temperatures.**

- However, the area under the two curves remains the same because area under the curves represents number of molecules.
- The rise in temperature increases the fraction of Molecules, having

higher speeds.

**Relationship between different types of Speeds:**

The different types of speeds are related as follows:-

$$\alpha : \bar{c} : U_{\text{r.m.s.}} :: 1 : 1.128 : 1.224$$

**Q.45 Define the following**

(a) Collision Number

(b) Mean free path

(c) Collision diameter

**Ans. Collision Number:**

- It is the number of collisions which a molecule registers with other molecules per second.
- It is given by the mathematical expression

$$\text{Collision Number} = \sqrt{2} \pi \sigma^2 \bar{c} N$$

$\bar{c}$  = average speed

$N$  = Number of molecules per  $\text{cm}^3$

$\sigma$  = Molecular diameter

**(b) Mean free Path:**

- The distance traveled by a molecule between two collisions is known as "free path"
- This distance varies time to time therefore an average of a large number of free path values, called "Mean free path" is taken.
- Thus mean free path is an average distance traveled by a Molecule between two successive collisions.
- It is denoted by ' $l$ '.
- It is given by the mathematical expression

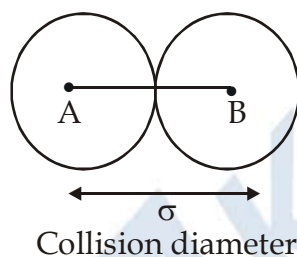
$$l = \frac{1}{\sqrt{2} \pi \sigma^2 N}$$

Here

$\sigma$  = Molecular diameter

N = No. of molecules per  $\text{cm}^3$

(c) **Collision diameter** : Molecular diameter  $\sigma$  :



#### Collision diameter

- When the gas molecules approach each other to collide, there is a distance of closest approach beyond which they cannot get closer.
- The distance between the centres of the molecules when they are closest to undergo a collision is called "Collision diameter or Molecular diameter".
- It is denoted by ' $\sigma$ '

**Q.46 Discuss the Principles used in the liquefaction of gases.**

**Ans.** According to kinetic theory of gases, the gases consists of small molecules separated from one another by large empty spaces (voids/holes).

- The molecules are in state of continuous rapid motion with Negligible attractive forces between them.
- When temp. is high and pressure is low, every molecule has independent existence.
- When temp. of gas is lowered, volume of gas and kinetic energy of molecules decreases.
- As a result, molecular motion becomes slow.



- the molecules come closer because they are unable to resist the attractive force which starts operating between them.
- As process of decreases of temperature, continues, the gas molecules go on moving closer and closer.
- the effect of bringing the gas molecules closer and closer can also be achieved by increasing pressure because this also causes increase in volume of gas.
- Thus liquefaction of gas can be achieved by decrease of temperature and by increase of Pressure.

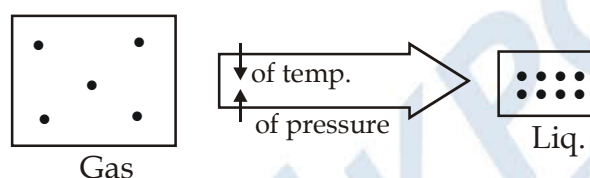


Fig. Liquefaction of gases

**Q.47 Write a short note on Joule-thomson effect in inversion temperature.**

**Ans.** When a compressed gas is allowed to expand through a small hole, cooling effect is caused and temperature falls.

- This is known as "Joule Thomson effect".
- Joule-thomson effect is observed below certain temperature. This temperature is called as "Inversion Temperature".
- It is denoted by  $T_i$ .
- Cooling effect is caused only during expansion if the temperature of the gas is less than its inversion temperature.
- If the temperature of the gas is greater than its inversion temperature then heating effect i.e. negative Joule Thomson effect is observed.
- Expansion of gas at its inversion temperature does not show cooling or heating effect i.e. at inversion temperature, Joule Thomson effect is zero.

**Q.48 Write a short note on Chemical Kinetic its scope.**

**Ans.** Chemical Kinetics is the science which deals with the rate of reactions and the factors which influences ( $\downarrow$  or  $\uparrow$ ) the rate of reaction.

Scope of chemical kinetics are as follows-

- (i) It reveals the minute events of reaction.
- (ii) It reveals about the optimum conditions for reaction like temp, pressure, by which we can obtain better yield of desired product.
- (iii) It is useful in all areas of human interest.

**Q.49** What do you mean by rate of reaction? Explain the factors on which it depends.

**Ans.** The rate of a reaction is related to the rate of decrease of concentration of the reactant or the rate of increase of concentration of the product.

$$\text{Rate of reaction} = \frac{\text{change In conc. of reactant}}{\text{time (taken for change)}}$$

The rate of reaction depends upon a number of factors which are as follows-

**(1) Nature of Reactant:** Rate of reaction depends upon the nature of reactant or bonds present between the reactant molecule. Rate of reaction increases for ionic compound and decreases for co-valent compound.

**(2) Concentration of reactant:** As conc. of reactants increases, the no. of molecules increases. As a result, collision increases and more molecules cross the activation energy and converts into product due to which rate of reaction increases.

**(3) Temperature:** On increasing the temperature, kinetic energy of molecules increases and more molecules collides and cross the activation energy which results in increase of rate of reaction.

**(4) Catalyst:** Catalyst are those substances which take part in the reaction without affecting the conc. of reactant. They choose that path which has less activation energy therefore rate of reaction increases.

**(5) Pressure:**  $3A \rightleftharpoons 2B$  if number of reactant molecules is more than the number of product molecules then pressure of forward reaction

increases. But if  $2A \rightleftharpoons 3B$  no. of product molecules are more than the number of reactant molecule then pressure of backward reaction increases due to which rate of backward reaction increases.

**Q.50 Derive the integrated rate law for zero order reaction.**

**Ans. Zero Order Reactions:** Those reactions in which rate of reactions doesn't depend on conc. of reactant. In such reactions, the rate may be determined by some other limiting factors such as amount of catalyst, used in catalytic reactions.



$$\text{At } t = 0 \quad a \quad 0$$

$$\text{At } t = t \quad a-x \quad x$$

Where  $a$  = initial conc. of reactant

$X$  = Conc. of reactant which decreases with time ' $t$ '

$a-x$  = after ' $t$ ' time remaining conc. of Reactant

Rate expression =

$$\boxed{\frac{dx}{dt} = k_0} \quad \dots(1)$$

on integrating eqn (1)

$$\boxed{x = k_0 t + c'}$$

$c'$  = integration constant applying boundary conditions for calculating value of constant.

At  $t = 0, X = 0$  then  $c' = 0$

On putting value of  $c'$  in eqn (2) we find

$$x = k_0 t \quad \dots(3)$$

Or

$$\boxed{k_0 = \frac{x}{t}} \quad \dots(4)$$

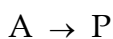
This is zero order rate constant ( $K_0$ )

**Q.51 Derive an integrated rate law for first order reaction.**

**Ans.** Those reactions in which rate of reaction is directly proportional to first power of concentration term.



$$\boxed{\text{Rate of Rx} \propto [A]} \quad \dots(1)$$



$$\text{at } t = 0 \quad a \quad 0$$

$$\text{at } t = t \quad d-x \quad x$$

$$\boxed{\frac{dx}{dt} = k_1[A]} \quad \dots(2)$$

$$\boxed{\frac{dx}{dt} = k_1[a-x]} \quad \dots(3)$$

$$\boxed{\frac{dx}{(a-x)} = k_1 dt} \quad \dots(4)$$

On integration

$$\boxed{-\ln(a-x) = k_1 t + c'} \quad \dots(5)$$

$c'$  = integration constant applying boundary conditions

$$\text{at } t = 0, \quad x = 0$$

$$\ln(a-0) = k_1(0) + c'$$

$$\boxed{-\ln a = c'} \quad \dots(6)$$

On putting value of  $c'$  in eqn (5) we get

$$\boxed{-\ln(a-x) = k_1 t + (-\ln a)} \quad \dots(7)$$

$$\boxed{-\ln(a-x) = k_1 t - \ln a} \quad \dots(8)$$

$$\boxed{-\ln(a-x) + \ln a = k_1 t} \quad \dots(9)$$

$$\boxed{\ln \left( \frac{a}{a-x} \right) = k_1 t}$$

$$\boxed{k_1 = \frac{1}{t} \ln \left( \frac{a}{a-x} \right)}$$

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

$\therefore$  This eqn (11) is called as integrated first order rate expression.

**Q.52 Derive the integrated rate law for second order reaction.**

**Ans.** Those reactions in which the rate of reaction depends on the second power of the concentration of a reactant or first power of each of the two reactant are called as "Second order Reactions"



$$\text{at } t = 0 \quad a \rightarrow 0$$

$$\text{at } t = t \quad a-x \rightarrow x$$

According to rate law

$$\boxed{\frac{dx}{dt} \propto [A]^2} \quad \dots(1)$$

$$\boxed{\frac{dx}{dt} = k_2[A]^2} \quad \dots(2)$$

at time 't'

$$\boxed{\frac{dx}{dt} = k_2[a-x]^2} \quad \dots(3)$$

$$\boxed{\frac{dx}{[a-x]^2} = k_2 \cdot dt} \quad \dots(4)$$

$$\boxed{\int_{(a-x)^2}^{dx} = k_2 \int dt} \quad \dots(5)$$

On integration we get

$$\boxed{\frac{1}{a-x} = k_2 t + c'} \quad \dots(6)$$

where  $c'$  = integration constant

On applying boundary condition i.e.

at  $t = 0, x = 0$

On putting these value in eqn (5) we get

$$\boxed{\frac{1}{a-0} = k_2 \cdot 0 + c'} \quad \dots(7)$$

$$\boxed{\frac{1}{a} = c'} \quad \dots(8)$$

On placing the value of  $c'$  in eqn (5) we get

$$\boxed{\frac{1}{a-x} = k_2 t + \frac{1}{a}} \quad \dots(9)$$

$$\frac{1}{a-x} - \frac{1}{a} = k_2 t \quad \dots(10)$$

$$\frac{a - (a-x)}{a(a-x)} = k_2 t \quad \dots(11)$$

$$\frac{a - a + x}{a(a-x)} = k_2 t \quad \dots(12)$$

$$\frac{x}{ta(a-x)} = k_2 \quad \dots(13)$$

$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \dots(14)$$

This is an expression for second order integrated rate law for a reaction when the concentration of both the reactants are equal the order with respect to a single reactant is two.

**Q.53 Explain the order of a reaction and describe the methods for determining the order of a reaction.**

**Ans.** The order of reaction is given by the number of atoms or molecules whose concentration changes during the chemical change.

Or

The order of reaction is given by the total number of molecules or atoms whose concentrations determine the velocity of the reaction.

There are many methods for determination of order of reaction.

**(1) Differential rate method:**

- In this type of method, order of reaction is determined by changing the concentration of the reactant.
- Suppose that initial conc. of the reactant is  $c_1$  it changes to the " $c_2$ " concentration.
- When conc. of reactant is  $c_1$  then rate of reaction.



$$\boxed{\frac{dx}{dt} = k_1 c_1} \quad \dots(1)$$

- When conc. of reactant is  $c_2$  then rate of reaction.

$$\boxed{\frac{dx}{dt} = k_2 c_2} \quad \dots(2)$$

- For Number of  $c_1$  molecules, rate of reaction

$$\boxed{\frac{dx}{dt} = k n c_1^n} \quad \dots(3)$$

For Number of  $c_2$  molecules rate of reaction

$$\boxed{\frac{dx_2}{dt} = k_n c_2^n} \quad \dots(4)$$

$$\boxed{\log \frac{dx_1}{dt} = \log [k_n c_1^n]} \quad \dots(5)$$

$$\boxed{\log \frac{dx_2}{dt} = \log [k_n c_2^n]} \quad \dots(6)$$

On adding eqn (5) & (6)

$$\log \frac{dx_1}{dt} = \log k_n + n \log c_1$$

$$\log \frac{dx_2}{dt} = \log k_n + n \log c_2$$

- - -

$$\log \frac{dx_1}{dt} - \log \frac{dx_2}{dt} = n \log c_1 - n \log c_2 \quad \dots(7)$$

$$\log \frac{dx_1}{dt} - \log \frac{dx_2}{dt} = n(\log c_1 - \log c_2) \quad \dots(8)$$

$$\frac{\log \frac{dx_1}{dt} - \log \frac{dx_2}{dt}}{\log c_1 - \log c_2} = n \quad \dots(9)$$

By this method we are able to determine, the value of  $n$  i.e. order of reaction.

### (2) Method of integration:

- This method is also called as Hit and trial method or Method of Empirical fit.
- Suppose the concentration of product be 'X' at any time 't', 'a' is the initial concentration of this species.
- We put the values of these data into each integrated forms of rate laws.
- When it gives constant values of the rate constant or that gives a straight line plot when function of X is plotted against time (t).
- If reaction is of first order, a plot of  $\log(a-x)$  versus time (t) yields a straight line.
- if the results do not fit the first order rate law, the values of 'x' and time (t) must be substituted into other rate laws i.e. second order and third order etc. until constant value of the rate constant is found.

### (3) Isolation Method:

- This type of method is used when more than one reactants are participating in the reaction.
- Suppose that when A, B & C reactant are reacting and forming the product P.
- To determine the order of reaction we taken two reactants in excess

and one in a very small amount.

- First of all suppose B and C is taken in excess amount so there is slight change in concentration of B and C is negligible and rate of reaction and order of reaction of A is determined.
- Similarly the order of reaction of B and C also determined.
- Now by adding all the three, order of whole reaction is calculated.

**Q.54 Name the experimental methods employed in determination of the rate constant. Explain one such method in details.**

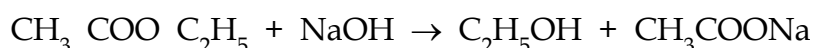
**Ans.** There are many methods which are employed in determination of the rate constant.

- (1) Conductometric Method
- (2) Potentiometric Method
- (3) Optical Method (Polarimetry)
- (4) Spectrophotometric method
- (5) Volumetric Method.

**(1) Conductometric Method:**

- This method is employed in those reactions in which number of ions increases or decreases.
- it is assumed that in case of dilute solutions, change in conductivity is proportional to the percentage of the reaction.
- the ionic conductivities of the hydrogen and hydroxyl ions are much larger than the conductivities of ions.
- Some examples of the reactions where this type of technique is applicable are as follows:-

Ester hydrolysis in alkaline solution (Saponification)



- As reaction proceeds, conductivity decreases because in this reaction

highly conducting hydroxyl ions ( $\text{OH}^-$ ) are replaced by acetate ions ( $\text{CH}_3\text{COO}^-$ ) of lower conductivity.

- Thus concentration of acetate ions increases with time in this reaction so conductivity decreases with time.
- The reactions are allowed to proceed for infinite time so that conductivity due to the formation of the products may be found as follows:

Let  $c_0$  = initial conductivity

$c_t$  = conductivity at time 't'

$c_\alpha$  = Conductivity of infinite time.

- Since, change in conductivity is proportional to percentage of reaction, the amount of reaction at time 't' is proportional to  $(c_t - c_0)$ .
- Total amount of reaction is proportional to  $(c_\alpha - c_0)$
- Fraction of reaction at time 't' is

$$\frac{c_t - c_0}{c_\alpha - c_0} \text{ which is equal to } \frac{x}{a}$$

- Now rate constant for first order process is

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad \dots(1)$$

- The change in conductivity after completion of the reaction is proportional to the initial concentration viz.

$$a \propto c_\alpha - c_0 \quad (\text{both are initial conc}) \quad \dots(2)$$

- Similarly conc. (x) is proportional to the change in conductivity at that time.

$$a \propto c_t - c_0 \quad \dots(3)$$

$$\text{So } a - x \propto \{(c_\alpha - c_0) - (c_t - c_0)\} \quad \dots(4)$$

$$a - x \propto c_\alpha - c_0 - c_t + c_0$$

$$a - x \propto c_\alpha - c_t \quad \dots(5)$$

Keep the values of 'a' from eqn (2) and a - x from eqn (5) in eqn (1) we get

$$k_1 = \frac{2.303}{t} \log \frac{c_\alpha - c_0}{c_\alpha - c_t} \quad \dots(6)$$

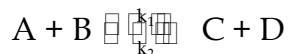
Now this is the rate constant in terms of conductivity.

**Q.55** How do you explain the increase in the rate with the increase in temperature? What is the equation which correlates the rate constant and the effect of temperature? Explain the terms involved.

**Ans.** It is a well established fact that the velocity of a chemical reaction whether the reaction is exothermic and endothermic increases with rise in temperature. In Homogenous reactions, the rate becomes doubled or trebled for each  $10^\circ$  rise of temperature. This increase in the reaction velocity with temperature is expressed in the form of temperature coefficient. According to Collision theory, as temperature increases from  $T^\circ\text{C}$  to  $(T + 10)^\circ\text{C}$ , Number of molecules having energy greater than as equal to threshold energy increases, thus, more molecules are effective in producing chemical changes. Hence the rate of reaction rises with rise in temperature.

**Arrhenious equation:** The Arrhenious equation that accounts for the effect of temperature on the rate of the reaction can be derived as follows-

Let consider a reversible Reaction



where  $k_1$  = forward rate constant

$k_2$  = backward rate constant

Rate of forward Rx<sup>4</sup> =  $k_1 [A] [B]$

Rate of Backward Rx<sup>4</sup> =  $k_2 [C] [D]$

When forward and backward reactions are in equilibrium then

$$k_1 [A] [B] = k_2 [C] [D]$$

Or

$$\frac{k_1}{k_2} = \frac{[C] [D]}{[A] [B]}$$

Since  $\frac{k_1}{k_2} = k$

$$\text{So } k = \frac{[C] [D]}{[A] [B]} \quad \dots(1)$$

From thermodynamics, von't Hoff equation is

$$\frac{d \ln k}{dt} = \frac{\Delta E}{RT^2} \quad \dots(2)$$

On placing the value of  $k$  i.e.  $\frac{k_1}{k_2}$  we get

$$\frac{d \ln \frac{k_1}{k_2}}{dt} = \frac{\Delta E}{RT^2} \quad \dots(3)$$

Or

$$\boxed{\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{\Delta E}{RT^2}} \quad \dots(4)$$

Van't Hoff proposed that equation (7) can be split up into following two equations as follows :

$$\therefore \Delta E = E_1 - E_2$$

$$\boxed{\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} + I} \quad \dots(5)$$

$$\boxed{-\frac{d \ln k_2}{dT} = -\frac{E_2}{RT^2} + I} \quad \dots(6)$$

These equations (5) & (6) are called as "Arrhenius equation"

Here 'I' is constant which does not depend upon the temperature. Thus eqn (5) & (6) can be written as follows -

$$\boxed{\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2}} \quad \dots(7)$$

$$\boxed{\frac{d \ln k_2}{dT} = \frac{E_2}{RT^2}} \quad \dots(8)$$

On integrating the (7) & (8) equation we get -

$$\boxed{\ln k_1 = -\frac{E_1}{RT} + c'} \quad \dots(9)$$

$$\boxed{\ln k_2 = -\frac{E_2}{RT} + c'} \quad \dots(10)$$

equation (9) & (10) can be written as follows in the form of exponential as follows -



$$k_1 = Ae^{-E_1/RT} \quad \dots(11)$$

$$k_2 = Ae^{-E_2/RT} \quad \dots(12)$$

However generalised form of these equations can be given by following equation-

$$k = Ae^{-E/RT} \quad \dots(13)$$

where A = frequency factor (Pre-exponential factor)

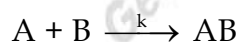
E = activation energy

Thus equation 13 is known as "integrated form of Arrhenius equation". This equation expresses the temperature dependence of k in terms of A and E. Both A & E are characteristics of the reaction.

**Q.56 Which are the reaction where collision theory yields rate constants similar to those calculated by other methods? Give the significance of the probability factors in this theory.**

**Ans.** According to collision theory, all collisions between the reacting molecules are not effective in producing a chemical change. There are only some collisions which lead to the reaction and to the formation of products. The reactant molecules should first acquire a minimum amount of energy called "threshold energy" and then collisions will occur to result in a chemical reaction. The collisions between molecules which are associated with energy less than threshold energy do not result in a chemical reaction therefore only a fraction of total molecules can have this energy.

Let us consider a simple reaction



in which let the number of molecules colliding per ml per sec be Z,  
Let 'q' be the fraction of molecules possessing the activation energy of

reaction.

Now rate constant for the reaction will be given by following equation-

$$k = Z \cdot Q \quad \dots(1)$$

Where  $Q = \frac{n'}{n}$

According to Maxwell's distribution law of molecular velocities-

$$\frac{n'}{n} = e^{-E/RT} = Q \quad \dots(2)$$

where  $n$  = total number of molecules.

$n'$  = number of molecules possessing activation energy.

Thus  $Q$  is the ratio of activated molecules & total number of molecules.

Substituting the value of  $Q$  from eqn (2) in eqn (1) we get

$$k = Z e^{-E/RT} \quad \dots(3)$$

$Z$  = Collision Number

This eqn (3) is an equation for rate constant derived by collision theory. Now we compare this equation with Arrhenius equation

$$k = A e^{-E/RT}$$

These two equations are similar with the only difference that here is 'A' in place of 'Z' (Frequency factor)

When reaction involves two different molecules, then the value of collision number ( $Z$ ) is given by

$$Z = \sigma^2 n^2 \left[ 8\pi RT \frac{(M_1 + M_2)}{M_1 M_2} \right]^{1/2} \quad \dots(4)$$

where  $M_1$  &  $M_2$  = Molecular weight

$\sigma$  = Mean of the molecules collision diameters of the two reactants A and B.

On substituting the value of (4) in eqn (3) we get

$$k = \sigma^2 n^2 \left[ 8\pi RT \left( \frac{M_1 + M_2}{M_1 M_2} \right) \right]^{1/2} \cdot e^{-E/RT} \quad \dots(5)$$

However, there is also a large number of such reactions for which experimental and theoretical values are not equal. There are also reaction where calculated rate constant is even  $10^5$  times higher than the experimental rate constant.

To explain it, it was observed that the assumption of activation energy being equivalent to kinetic energy in collision theory. Such assumption is valid for only rigid spheres.

This concept can not be apply for complex molecules because they possess rotational energy as well as vibrational energy along with kinetic energy. Therefore other rate constant or modified collision theory is given as follows-

$$k = P \cdot Z e^{-E/RT}$$

where P = Probability factor of molecules which get activated.

$\sigma$  = mean collision diameter.

$M_1 + M_2$  = Masses of colliding molecules.

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