

## Department of Chemistry

**Attention: All the students of Semester II having Chemistry as General Paper ( GE 2 and C 2)**

The concerned students are hereby informed that the following items from their respective syllabi has to be taken care of for their Semester II Examination, 2020. The students should consult **any text book** they possess, even books from their Higher Secondary classes may be helpful.

Paper GE2T and COR2T in Chemistry contains two sections.

Section A: *Physical Chemistry-I* which includes three different states of matter (gaseous, liquid and solid) and chemical kinetics.

**From the first part special care has to given for the Kinetic theory of gases and real gases.**

1. Maxwell's distribution of speed and kinetic energy  
Only the equations for such distributions, their physical interpretations including graphical representations etc. are important.
2. Collision Frequency (binary collisions); Collision diameter; mean free path and its dependence on pressure and temperature.
3. Principle of equipartition of energy, molar heat capacity.
4. Deviation of gases from ideal behaviour; compressibility factor; Boyle temperature; Andrew's and Amagat's plots; van der Waals equation and its features; Existence of critical state, Critical constants in terms of van der Waals constants;

### **Liquids**

1. Definition of Surface tension and viscosity; their dimensions.
2. Effect of temperature on surface tension and coefficient of viscosity of a liquid (qualitative treatment only)

### **Solids**

Laws of Crystallography - Law of constancy of interfacial angles, Law of rational indices; Miller indices of different planes and interplanar distance, Bragg's law.

### **Chemical Kinetics**

1. Order and molecularity; rate constants; Rates of First, second order reactions and their differential and integrated forms (with derivation); Pseudo first order reactions;
2. Determination of order of a reaction by half-life and differential method;
3. Temperature dependence of rate constant; Arrhenius equation, energy of activation;

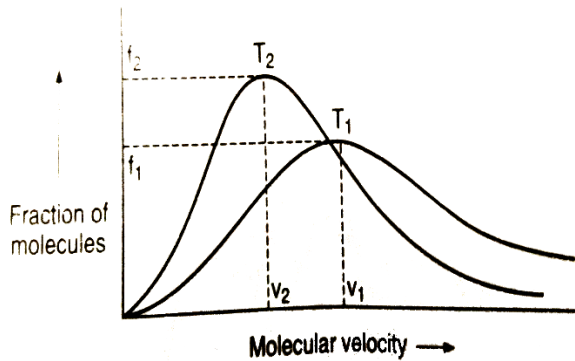
## KINETIC THEORY OF GASES AND REAL GASES

### 1. The distribution of molecular speed: Maxwell's equation

The fraction of molecules having speeds between  $c$  and  $c + dc$  was expressed by Maxwell (using the theory of probability) as  $\frac{dN}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 e^{-Mc^2/2RT} dc$

Where,  $dN$  is the no. of molecules having speeds between  $c$  and  $c + dc$  among total  $N$  no. of molecules at temperature  $T$ .  $M$  is the molecular weight of the gas.

- For any gas, the fraction  $dN/N$  has a constant value at a certain fixed temperature.
- A typical Maxwell's plot [ $\frac{1}{N} \frac{dN}{N}$  (on y-axis) vs  $c$  (on x-axis)] at two temperatures ( $T_1 > T_2$ ) is as follows



- Each curve passes through a maximum at a speed known as most probable speed  $c_{mp}$ .
- The no. of molecules having very high or very low speeds is small, and majority of the molecules move with intermediate speeds.

- $c_{mp} = \sqrt{\frac{2RT}{M}}$ ;  $c_{rms} = \sqrt{\frac{3RT}{M}}$ ;  $c_{av} = \sqrt{\frac{8RT}{\pi M}}$

### 2. Molecular Collisions

Mean free path ( $\lambda$ ): The average distance travelled by a molecule between two successive molecular collisions.

$$\text{So, } \lambda = \frac{\text{average distance travelled per unit time}}{\text{no. of collisions made by a single molecule per unit time}} = \frac{1}{\sqrt{2} \pi \sigma^2 N^*}$$

Where,  $\sigma$  is the molecular diameter and  $N^*$  is the no. of molecules per unit volume.

$$\text{Since } N^* \propto \frac{p}{T} \Rightarrow \lambda \propto \frac{T}{p}$$

Therefore,  $\lambda \propto T$  at constant  $p$  and  $\lambda \propto \frac{1}{p}$  at constant  $T$

No. of collisions suffered by a single gas molecule with the other molecules present per unit volume of the pure gas, per unit time ( $Z_1$ ) is expressed as

$$Z_1 = \frac{\text{average distance travelled per unit time}}{\text{average distance between collisions}} = \frac{\bar{c}}{\lambda} = \sqrt{2} \pi \sigma^2 \bar{c} N^*$$

$$\text{Total no. of bimolecular collision per unit volume per unit time } Z_{11} = \frac{1}{2} Z_1 N^* = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{c} N^{*2}$$

### 3. Principle of equipartition of energy

The total energy of a molecule can be assumed to be divided equally among different degrees of freedom (translational, rotational and vibrational), the amount for each degree of freedom being  $\frac{1}{2} kT$  per molecule ( $k$  is the Boltzmann constant).

For a molecule containing  $N$  atoms, there are in all  $3N$  degrees of freedom.

Translational degrees of freedom = 3

Rotational degrees of freedom = 2 (for a linear molecule) and 3 (for a non-linear molecule)

Remaining  $3N - 5$  (for a linear molecule) and  $3N - 6$  (for a non-linear molecule) degrees of freedom for the vibrational motion.

Total average energy of one mole of the gas is

$E = \frac{3}{2} RT + RT + (3N - 5) RT$  (for a linear molecule) and  $E = \frac{3}{2} RT + \frac{3}{2} RT + (3N - 6)RT$  (for a non-linear molecule)

#### 4. Real gases

van der Waals equation:  $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$  for  $n$  moles of a real gas.

The term  $a$  is constant characterizing the nature and extent of intermolecular interactions per mole of the gas. Another constant  $b$  is related to the molecular volume.

- CGS unit of  $a$  is  $atm. (dm^3)^2 mol^{-2}$  and that of  $b$  is  $dm^3 mol^{-1}$
- Critical constants:  $p_c = \frac{a}{27b^2}$  ;  $T_c = \frac{8a}{27Rb}$  ;  $V_c = 3b$  ,
- Boyle temperature:  $T_B = \frac{a}{Rb}$

## SURFACE TENSION AND VISCOSITY COEFFICIENT OF LIQUIDS

### SURFACE TENSION

**Definition:** Force acting tangentially to the surface and perpendicular to a line of unit length drawn on the surface.

**Symbol:**  $\gamma$

**Unit :** CGS unit -----dyne/cm

SI unit-----N/m

**Origin:** Intermolecular force of attraction between liquid molecules

**Explanation:** In the interior of the liquid , molecule is surrounded on all sides by other liquid molecules. Hence force of attraction on all sides cancel one another and net force on molecule is zero. But at the surface, molecules have a downward pull, as there are more liquid molecules as compared to vapor phase molecules. Therefore surface tends to contract.

**Factors on which surface tension depend:** 1. Nature of liquid 2. Temperature

**Temperature Dependence of Surface Tension:** As temperature increase, force of attraction between liquid molecules decrease, hence surface tension decreases.

### VISCOSITY

**Definition:** It is the measure of the resistance to flow of a liquid and acts in a direction opposite to flow.

**Explanation:** The layer of liquid in contact with the tube surface is stationary with zero velocity. As distance of liquid layer increases with distance from surface of tube, its velocity increases. As adjacent layers of different velocity move past one another each exerts a frictional resistance force on the other layer. This slows down the faster moving layers resulting in viscosity.

**Newton's law of viscosity:**  $F = -\eta A \left(\frac{dv}{dx}\right)$ , where F = viscous force acting on layer, A= area of layer,  $\left(\frac{dv}{dx}\right)$  = velocity gradient,  $\eta$  = coefficient of viscosity

### Coefficient of viscosity

$$\eta = \frac{F}{A\left(\frac{dv}{dx}\right)}$$

**Definition:** Tangential force per unit area required to maintain unit velocity gradient

**Symbol:**  $\eta$

**Unit :** CGS unit -----dyne-sec/cm<sup>2</sup> or Poise

SI unit-----N-sec/m<sup>2</sup> or Pascal sec

**Factors on which viscosity depend:** 1. Nature of liquid 2. Temperature

**Temperature Dependence of Viscosity coefficient:** As temperature increase, internal friction between fluid layers decrease, fluidity increase and viscosity coefficient decreases.

### Comparison between viscosity of liquids and gasses:

Gases	Liquids
1. Occurs due to transport of momentum between layers of gas	1. Occurs due to internal friction resulting from intermolecular force of attraction between molecules
2. Molecules move from one layer to another	2. Molecules do not migrate between layers
3. Coefficient of viscosity increases with temperature	3. Coefficient of viscosity decreases with temperature

**Notes on other topics will be uploaded in future**