

- 1 mole of any gas at 273 K (0°C) and 1 atm has a volume of 22.4 L. The conditions of 273 K and 1 atm are the standard temperature and pressure (STP).

### KINETIC THEORY OF GASES

- Given by Bernoulli in 1738 and developed by Clausius, Maxwell, Kronig and Boltzmann in 1860. Postulates are :
  - The dimensions of the particles are negligibly small compared to the average distance between them.
  - The molecules of the gas are in constant random, rapid and chaotic motion. The measured gas pressure is due to the collisions of the gas molecules with the surfaces of containing vessels.
  - All collisions are perfectly elastic, and the molecules have no interactions apart from these collisions.
  - The average kinetic energy of the molecules is related to the temperature of the gas. The greater the temperature, the greater the kinetic energy.

- Kinetic gas equation and kinetic energy**

$$PV = \frac{1}{3} mnC_{rms}^2$$

where  $P$  = Pressure of the gas

$V$  = Volume of the gas

$m$  = Mass of a gas molecule

$n$  = Number of gas molecules

$C_{rms}$  = Root mean square velocity for 1 mole of the gas,

- For 1 mole of the gas  $PV = RT$  and  $n = N$  where  $N$  = Avogadro's number

$$PV = \frac{1}{3} mnC_{rms}^2 \quad \text{or} \quad \frac{2}{3} \times \frac{1}{2} mNC_{rms}^2 = RT$$

$$\text{Now} = \frac{1}{2} mNC_{rms}^2 = \text{kinetic energy per mole}$$

$$\therefore \frac{2}{3} K.E. = RT \quad \text{or} \quad K.E. = \frac{3}{2} RT$$

- Average  $K.E.$  per molecule =  $\frac{\text{Average } K.E. \text{ per mole}}{\text{Avogadro's number}}$

$$= \frac{\frac{3}{2} RT}{N} = \frac{3}{2} kT$$

where  $k = \frac{R}{N}$ , and  $k$  is called Boltzmann constant. Its numerical value is  $1.38 \times 10^{-16}$  erg  $K^{-1}$  molecule $^{-1}$ .

### DIFFERENT TYPES OF MOLECULAR VELOCITIES

Most probable velocity ( $C_{mp}$ )	Velocity possessed by maximum number of molecule.	$C_{mp} = \sqrt{\frac{2RT}{M}}$
Average velocity ( $C_{av}$ )	Mean of different velocities possessed by the molecules of a gas.	$C_{av} = \frac{C_1 + C_2 + \dots + C_n}{n}$ $= \sqrt{\frac{8RT}{\pi M}}$

Root mean square velocity ( $C_{rms}$ )	Square root of the mean of squares of the velocities possessed by all the molecules present.	$C_{rms} = \sqrt{\frac{C_1^2 + C_2^2 + \dots + C_n^2}{N}}$ $= \sqrt{\frac{3RT}{M}}$
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- Relation between  $C_{mp}$ ,  $C_{av}$ ,  $C_{rms}$

$$C_{mp} : C_{av} : C_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= 1 : 1.128 : 1.224$$

$$C_{av} = 0.9213 \times C_{rms}, \quad C_{mp} = 0.8165 \times C_{rms}$$

### Illustration 4

Calculate most probable velocity, average velocity and root mean square velocity for  $N_2$  at  $15^\circ C$ .

**Soln.:** Given,  $T = 288$  K

$$C_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 288}{28 \times 3.14 \times 10^{-3}}} = 466.76 \text{ m/sec}$$

$$C_{rms} = \frac{C_{av}}{0.9213} = 506.63 \text{ m/sec}$$

$$V_{np} = C_{rms} \times 0.8165 = 506.63 \times 0.8165 = 413.67 \text{ m/sec}$$

### DEVIATION FROM IDEAL BEHAVIOUR OR VAN DER WAALS' EQUATION

- In 1873, van der Waals proposed his famous equation of state for a non-ideal gas or real gas. van der Waals suggested that the deviations of gases from ideal behaviour are due to following two faulty assumptions in the kinetic theory of gases.

- Actual volume of the gas molecule is negligible as compared to the volume of the gas.
- Intermolecular attractions are not present in gases.

- Volume correction :** In real gases, a part of the total volume is occupied by the gas molecules. Hence, real volume of gas = Actual volume of container – volume occupied by  $N$  molecules in motion.

$$V_i = V - b \quad \text{for one mole of gas}$$

$$V_i = V - nb \quad \text{for } n \text{ mole of gas}$$

where  $b$  is termed the 'excluded volume' or 'co-volume'. It is constant and characteristic for each gas.

$$b = \left(\frac{4}{3}\pi r^3\right) \times 4N \quad [\text{where } r = \text{radius of gas molecule,}$$

$$N = \text{Avogadro's number}]$$

- Pressure correction :** In order to take into account the effect of intermolecular forces of attraction.
- van der Waals noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules,  $n/V$ .

Thus,

$$P(\text{actual}) = P(\text{ideal}) - n^2 a/V^2$$

$$\text{or } P(\text{ideal}) = P(\text{actual}) + n^2 a/V^2$$

' $a$ ' is a constant which depends upon the nature of the gas,  $V$  is the volume of 1 mole of gas.

## States of Matter : Gases and Liquids

Combining the two corrections, for 1 mole of gas

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

For  $n$  mole of gas  $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

- At low pressures, volume correction for 1 mole of gas is negligible,

$$\therefore b = 0$$

The gas equation can be written as

$$\left(P + \frac{a}{V^2}\right)V = RT \text{ or } Z = \frac{PV_m}{RT} = 1 - \frac{a}{V_m RT}$$

where  $V_m$  = molar volume

$Z$  is known as the **compressibility factor**.  $Z$  is 1 for ideal gases.

- At higher pressures, the pressure correction for 1 mole of gas is negligible.

$$\therefore \frac{a}{V^2} = 0$$

$$\text{or } (P + 0)(V - b) = RT \text{ or } P(V_m - b) = RT$$

$$\text{or } PV_m = RT + Pb \quad \bullet, Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$$

### Compressibility Factor

- Compressibility factor,  $Z = \frac{PV}{RT}$ , for 1 mole of a gas.

For ideal gas  $Z = 1$  as  $PV = RT$

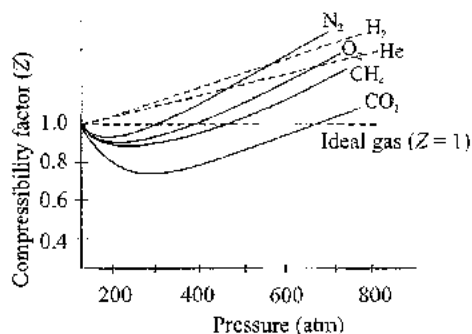
but for real gases  $Z \neq 1$  as real gases do not obey ideal gas equation.

- When  $Z > 1$ , the gas shows positive deviation from ideal behaviour and is less compressible than expected from ideal behaviour. ( $V_m > 22.4$  L at STP).

$Z > 1$  corresponds to repulsive forces between electron clouds of molecules of gas.

- When  $Z < 1$ , the gas shows negative deviation and is more compressible than expected from ideal behaviour ( $V_m < 22.4$  L at STP).  $Z < 1$  corresponds to attractive forces between molecules.

Greater the difference in the value of  $Z$  from unity, greater are the deviations from ideal behaviour.



### Illustration 5

The density of water vapour is  $5.970 \times 10^{-4}$  g/cc at  $100^\circ\text{C}$  and 1 atm pressure. What is the molar volume and compare it with ideal gas value? Also determine the compressibility factor.

**Soln.:** Volume of  $5.970 \times 10^{-4}$  g water vapours = 1 cc

$\therefore$  Volume of 18 g water vapours *i.e.*, molar volume at given conditions

$$= \frac{1}{5.97 \times 10^{-4}} \times 18 = 30150 \text{ cc} = 30.15 \text{ L}$$

Molar volume for ideal gas at given conditions

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 373}{1} = 30.62 \text{ L}$$

$$\text{Compressibility factor, } Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} = \frac{30.15}{30.62} = 0.986$$

### LIQUEFACTION OF GASES

- Whenever the intermolecular forces of attraction in a gas increase to a level that molecules bind together, then liquefaction of gas takes place. Thus, a gas can be liquefied either by cooling or by applying appreciable pressure or by combined effect of both.

- Critical temperature ( $T_c$ ):** It is a particular temperature of a gas above which the gas can not be liquefied, however high pressure is applied on the gas.

$$T_c = \frac{8a}{27bR}$$

- Critical pressure ( $P_c$ ):** The minimum pressure required to liquefy a gas at critical temperature is called critical pressure.

$$P_c = \frac{a}{27b^2}$$

- Critical volume ( $V_c$ ):** The volume occupied by 1 mole of a gas at critical temperature and critical pressure is called critical volume.

$$V_c = 3b$$

All the three quantities are collectively known as **critical constants** of a gas.

- Relation between three critical constants**

$$P_c V_c = \frac{3}{8} RT_c \text{ or } \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

*i.e.*,  $Z < 1$  at critical point.

At the critical point, densities of substances in gaseous state and liquid state are same and there is no distinction between the two states.

### Illustration 6

The critical constant for water are  $374^\circ\text{C}$ , 218 atm and 0.0566 litre  $\text{mol}^{-1}$ . Calculate  $a$ ,  $b$ , and  $R$ .

**Soln.:** Given,  $T_c = 374^\circ\text{C} = 374 + 273 = 647$  K,  $P_c = 218$  atm  
 $V_c = 0.0566$  litre  $\text{mol}^{-1}$

$$\therefore b = \frac{V_c}{3} = \frac{0.0566}{3} = 0.0189 \text{ L mol}^{-1}$$

$$a = 3P_c V_c^2 = 3 \times 218 \times (0.0566)^2 = 2.095 \text{ L}^2 \text{ atm mol}^{-2}$$

$$R = \frac{8 P_c V_c}{3 T_c} = \frac{8 \times 218 \times 0.0566}{3 \times 647} = 0.05086 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

- van der Waals constant 'a' and liquefaction :** Liquefaction of a gas is related to strength of intermolecular forces of attraction of that gas. van der Waals constant 'a' is a measure of such attractive forces. Greater the value of 'a' greater are the intermolecular forces of attraction. Hence, more easily the gas is liquefied i.e., higher would be the critical temperature of that gas. It is found that 'a' is directly related to critical temperature ( $T_c$ ). With the increase in value of 'a', critical temperature also increases.

### LIQUID STATE

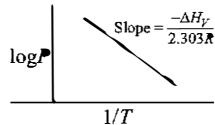
- Liquid state is intermediate between the gas and solid state. In liquids the molecules are close enough, so that there are considerable intermolecular forces of attraction. Liquids have definite volume like solids but no definite shape. Liquids possess fluidity like gases but incompressibility like solids.
- Vapour pressure :** The pressure exerted by vapours of the liquids present above the liquid in equilibrium with the liquid at that temperature. Vapour pressure of a liquid depends upon the nature of liquid and temperature. Vapour pressure is high for those liquids which have weaker intermolecular attractive forces, so that molecules can easily leave the liquid to vapour state. With the increase of temperature, vapour pressure increases.

$$P = A \exp(\Delta H_v / RT),$$

$$\log P = \log A - \frac{\Delta H_v}{2.303RT}$$

$A = \text{constant}$

$H_v = \text{enthalpy of vapourisation}$



### Coefficient of Viscosity

- It is the force per unit area required to maintain a velocity difference of unity between the two parallel layers in the liquid which are unit distance apart.
- The force of attraction between two layers of liquid each having area of  $A$ , separated by a distance of  $dx$  and having velocity difference of  $dv$  is given as

$$f \propto A \frac{dv}{dx} \Rightarrow f = \eta A \frac{dv}{dx}$$

Where,  $\eta = \text{coefficient of viscosity}$

$$\eta = \frac{f dx}{A dv}$$

- Viscosity of liquid decreases with increase of temperature whereas increases with decrease of temperature.
- The coefficient of viscosity of a liquid varies with temperature according to the following equation :  
 $\eta = A e^{E_a/RT}$  (Arrhenius equation)  
 Where  $A$  is a constant and  $E_a$  is activation energy for viscous flow which is constant for a particular liquid.
- The reciprocal of coefficient of viscosity is known as fluidity of the liquid.

$$\phi = \frac{1}{\eta}$$

### Surface Tension

- It is the force acting at right angle to the surface along one centimetre length of the surface of liquid at rest. It may also be defined as the force required to rupture the surface of liquid along unit length. Surface tension of liquid decreases with increase of temperature and becomes zero at its critical temperature. It is expressed in  $\text{Jm}^{-2}$  or  $\text{Nm}^{-1}$ .