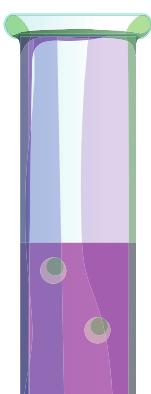




# States of Matter

CH 5 Chemistry | Class 11

Notes + 10 Years Integrated PYQ's





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## Gaseous State :-

Matter can be classified into three categories depending upon its physical state namely solid, liquid and gaseous states.

### # Distinction Between Three States of Matter :-

S.No.	Solids	Liquids	Gases
1.	Particles are very closely packed	Particles are loosely packed	Particles are very loosely packed
2.	Voids are extremely small.	Voids are relatively larger	Voids are very large
3.	Inter particle forces are large	Inter particle forces are intermediate	Interparticle forces are negligible.
4.	Particle motion is restricted to vibratory motion	Particle motion is very slow	Particle motion is very rapid and also random

### # Measurable Properties of Gases :-

Mass, Volume, temperature are the important measurable properties of Gases.

⇒ Mass:- The mass of the gas is related to the no. of moles as  $n = \frac{w}{M}$

⇒ Volume :- Since gases occupy the entire space available to them, therefore the gas volume means the volume of the container in which the gas is enclosed.

⇒ Pressure :- The force exerted by the gas per unit area on the walls of the container is equal to its pressure.

⇒ Temperature :- Temperature is defined as the degree of hotness.

### # Gas laws :-

⇒ Boyle's law :- The changes in the volume of a gas by varying pressure at a constant temperature of a fixed amount of gas was quantified by Robert Boyle in 1662. The law was named after his name as Boyle's law. It states that:-

{ The volume of a given mass of a gas  $\propto \frac{1}{\text{pressure at a constant}}$  }

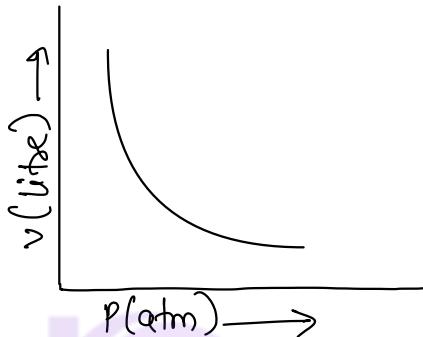
$$P \propto \frac{1}{V} \quad (n, T \text{ constant})$$

$$V \propto \frac{1}{P} \quad (n, T \text{ constant})$$

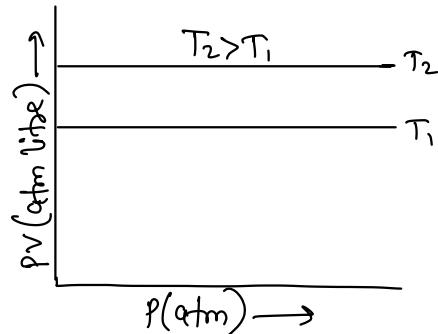
i.e.  $P = k/V$  (where  $k$  is the constant proportionality)  
or  $PV = k$  (Constant)

$$P_1 V_1 = P_2 V_2$$

⇒ Graphical Representation of Boyle's law :-



(a) Plot of  $V$  against  $P$



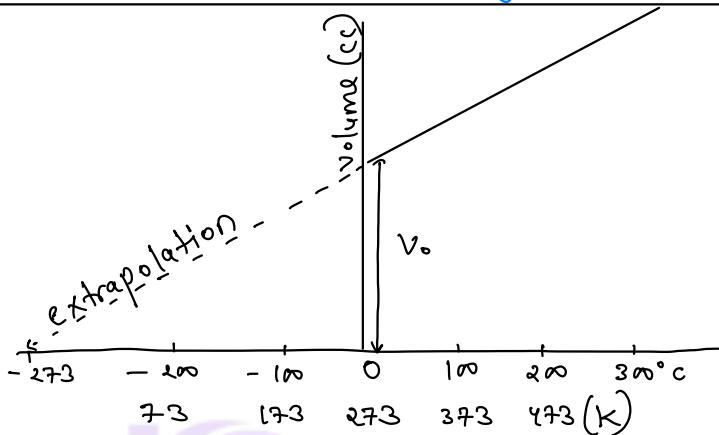
(b) Plot of  $PV$  against  $P$

⇒ Charles's law :- for a fixed amount of a gas at constant pressure, the gas expands as temperature increases.

$$\text{In } PV = nRT \quad V = \left(\frac{nR}{P}\right)T \quad P = \text{constant}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \begin{matrix} V \propto T \\ (\text{Pressure and Mass Constant}) \end{matrix}$$

⇒ Graphical Representation of Charles's law :-



⇒ Combined Gas Equation :-

The Boyle's and Charles's law can be combined to give a relationship between the three variables  $P, V$  and  $T$ .

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad PV = nRT \text{ or } \left( \frac{PV}{T} = nR \right)$$

↓  
constant

⇒ Avogadro's law :- The Avogadro's law states that at a given temperature and pressure, the volume of a gas is directly proportional to the amount of gas i.e.

$$V \propto n \quad (P \text{ and } T \text{ constant})$$

or  $V = \text{Constant} \times n$

$n$  is the amount of the substance  
 1 mol of any gas at  $0^\circ\text{C}$  and under 1 atm  
 pressure occupies  $22.4 \times 10^{-3} \text{ m}^3$  or 22.4 litre

### ⇒ Ideal Gas Equation :-

A gas that would obey Boyle's and Charles' law under all the conditions of temperature and pressure is called an Ideal Gas.

$$\left. \begin{array}{l} P V = n R T \end{array} \right\}$$

This is called ideal gas eqn

where  $R$  is the constant of proportionality or universal gas constant

The value of  $R$  was found out to be

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

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

$$R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

### ⇒ Relation between Molar mass and density (from ideal gas equation)

$$n = \frac{W}{M}$$

$$P = d \frac{RT}{M}$$

$$P = \frac{nRT}{V}$$

$$d = \frac{PM}{RT}$$

$$P = \frac{W}{V} \frac{RT}{M}$$

Eg:- At which of the four conditions, the density of nitrogen will be the largest?



Sol<sup>n</sup>:- Density of a gas is given  $\rho = \frac{PM}{RT}$ . Obviously the choice that has greater  $\frac{P}{T}$  would have greater density.  
Hence, (B) is correct

⇒ Gay Lussac's Law (temperature pressure law):

It state that pressure of the given air mass a gas is directly proportional to the Kelvin temperature at constant volume.

P & T (n, V are constant)

$$\frac{\rho}{T} = k = \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

⇒ Pay-load :

When a balloon is buoyant, it can take along some weight into the upper atmosphere. The maximum weight a balloon can carry along is called its payload.

Pay load = wgt of the air displaced - (wgt of the balloon  
                  + wgt of the gas it  
                  contains)

**Eg:-** When 2 g of gaseous substance A is introduced into an initially evacuated flask kept at 25°C, the pressure is found to be 1 atm. The flask is evacuated and 3 g of B is introduced. The pressure is found to be 0.5 atm at 25°C. Calculate the ratio  $\frac{M_A}{M_B}$  (m - molecular weight)

$$\text{Sol}^n:- \quad PV = \frac{m}{M} RT$$

$$\frac{P_A}{P_B} = \frac{\frac{m}{M_A}}{\frac{m}{M_B}} \times \frac{M_B}{m_B} \quad (\text{because } V, R \text{ and } T \text{ are constants})$$

$$\frac{1}{0.5} = \frac{2}{M_A} \times \frac{M_B}{3}$$

$$\frac{M_A}{M_B} = \frac{1}{3}$$

### ⇒ Dalton's law of Partial Pressure:-

The relation between the pressure of the mixture of non-reacting gases enclosed in a vessel to their individual pressure is described in the law. The law was given by John Dalton in 1807. It states that:-

At constant temperature, the pressure exerted by a mixture of two or more non-reacting gases enclosed in a definite volume, is equal to the sum of the individual pressures which each gas

would exert if present alone in the same volume  
The individual pressures of gases are known as  
partial pressures

If  $P$  is the total pressure of the mixture  
of non-reacting gases at temperature  $T$  and  
volume  $V$ , and  $p_1, p_2, p_3 \dots$  represent the  
partial pressures of the gases, then

$$P = p_1 + p_2 + p_3 + \dots \quad (T, V \text{ are constant})$$

### ⇒ Partial Pressure in terms of Mole fraction:-

Mole fraction  $x$  defined the amount of a substance  
in a mixture as a fraction of total amount of  
all substances - If  $n$ , moles of a substance is  
present in  $n$  moles of the mixture, then mole  
fraction of the substance,  $x_i = \frac{n_i}{n}$

If  $p_{N_2}$  is the partial pressure of nitrogen the  
mixture of  $SO_2$  and  $N_2$ . Then,

$$p_{N_2} = n_{N_2} \times \frac{RT}{V} \quad (n_{N_2} = \text{no. of moles of } N_2)$$

$$\text{and } P_{\text{mixture}} = (n_{N_2} + n_{SO_2}) \times \frac{RT}{V}$$

Dividing we get,

$$\frac{p_{N_2}}{P_{\text{mixture}}} = \left( \frac{n_{N_2}}{n_{N_2} + n_{SO_2}} \right) = x_{N_2}$$

$$\text{Or, } p_{N_2} = x_{N_2} \times P_{\text{mixture}}$$

Eg:- At an under water depth of 250 ft, the pressure is 8.38 atm. What should be the mole percent of oxygen in the diving gas for the partial pressure of oxygen in the mixture to be 0.21 atm, the same as it is in air at 1 atm?

Sol:- Since  $P_{O_2} = X_{O_2} \times P_{\text{total}}$  then  $X_{O_2} = \frac{P_{O_2}}{P_{\text{total}}}$

$$X_{O_2} = \frac{0.21}{8.38} = 0.025$$

So, the diving gas should contain 2.5% of O<sub>2</sub>

### → Graham's law of Diffusion / Effusion:-

The ability of a gas to spread and occupy the whole available volume irrespective of other gases present in the container is called diffusion.

Effusion is the process by which a gas escapes from one chamber of a vessel through a small opening or an orifice  $\propto = \frac{\text{volume diffused}}{\text{time taken}} = \frac{V}{T}$

The law states under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square roots of their densities.

$r \propto \frac{1}{\sqrt{d}}$  where r is the rate of diffusion and d is the density of the gas

Now, if there are two gases A and B having  $r_1$  and  $r_2$  as their rates of diffusion and  $d_1$  and  $d_2$  their densities respectively then,

$$r_1 \propto \frac{1}{\sqrt{d_1}} \text{ and } r_2 \propto \frac{1}{\sqrt{d_2}} \text{ or } \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad (\text{at same T and P})$$

$$\frac{r_1}{r_2} = \sqrt{\frac{\frac{M_2}{2}}{\frac{M_1}{2}}} = \sqrt{\frac{M_2}{M_1}} = \frac{V_1}{V_2} \frac{T_1}{T_2}$$

Here  $M_1$  and  $M_2$  are the molecular masses of the gases having densities  $d_1$  and  $d_2$  respectively. Graham's law of diffusion also holds good for effusion.

### Effect of Pressure on State of Diffusion:

The rate of diffusion ( $r$ ) of a gas at constant temperature is directly proportional to its pressure

$$r \propto p$$

$$r \propto \frac{1}{\sqrt{M}}$$

} → at constant temperature

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}}$$

Eg:- Which of the two gases ammonia and hydrogen chloride will diffuse faster and by what factor?

Sol:-

$$\frac{r_{NH_3}}{r_{HCl}} = \left( \frac{M_{HCl}}{M_{NH_3}} \right)^{\frac{1}{2}}$$
$$= \left( \frac{36.5}{17} \right)^{\frac{1}{2}} = 1.46 \text{ or } r_{NH_3} = 1.46 r_{HCl}$$

Thus, ammonia will diffuse 1.46 times faster than hydrogen chloride gas.

## # Kinetic Molecular theory of Gases:-

### Postulates of the Model :-

- A gas consists of a large no. of identical molecules of mass m. The dimensions of these molecules are very small compared to the space between them. Hence, the molecules are treated as point masses.
- There are practically no attractive forces between the molecules. The molecules therefore move independently.
- The molecules are in a state of ceaseless and random motion, colliding with each other and with the walls of the container. The direction

of their motion changes only on collision. These collisions are known as elastic collisions in which the energy and momenta of the molecules are conserved. In non-elastic collisions these quantities are not conserved.

- The pressure of a gas is the result of collision of molecules with the wall of the container.
- The average kinetic energy of the colliding molecules is directly proportional to its temperature.

# Velocities of Gas molecules:

⇒ Average Velocity:

As per kinetic theory of gases, each molecule is moving with altogether different velocity. Let 'n' molecules be present in a given mass of gas, each one moving with velocity  $v_1, v_2, v_3 \dots v_n$ . The average velocity or  $v_{av}$  = average of all such velocity terms.

$$\text{Avg. Velocity} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n} = \frac{n_1 v_1 + n_2 v_2 + n_3 v_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

$$v_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8P}{\pi d}}$$

## ⇒ Root mean Square Velocity :-

Maxwell proposed the term  $U_{rms}$  as the square root of means of square of all such velocities

$$U_{rms}^2 = \frac{U_1^2 + U_2^2 + U_3^2 + \dots}{n} = \frac{n_1 U_1^2 + n_2 U_2^2 + n_3 U_3^2 + \dots}{n_1 + n_2 + n_3}$$

$$\text{Also } U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

## ⇒ Most probable velocity :-

It is the velocity which is possessed by maximum no. of molecules.

$$V_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{d}}$$

$$\text{Furthermore } V_{mp} : V_{av} : V_{rms} :: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$\sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$1 : 1.228 : 1.224 \longrightarrow \text{Important ratio}$$

$$\text{Also } V_{av} = U_{rms} \times 0.9213$$

## ⇒ Kinetic Energy of Gas:-

As per kinetic eq<sup>n</sup>  $PV = \frac{1}{3} m n u^2_{rms}$

For 1 mole  $m \times n = \text{Molecular Mass (M)}$

$$\therefore PV = \frac{1}{3} M u^2_{rms} = \frac{2}{3} \times \frac{1}{2} M u^2 = \frac{2}{3} \times \text{K.E./mole or } \frac{\text{K.E.}}{\text{mole}}$$

$$\text{Also, } \frac{\text{K.E.}}{\text{molecule}} = \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} kT$$

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

where  $k$  is the Boltzmann Constant  $(k = \frac{R}{N_A})$

**Eg :-** Calculate rms speed of O<sub>2</sub> at 273 K and  $2 \times 10^5$  Pa pressure. The density of O<sub>2</sub> under these conditions is 1.42 kg m<sup>-3</sup>

**Sol :-** Data are given in SI units

$$u_{rms} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 10^5}{1.42}} = 459.63 \text{ m sec}^{-1}$$

## ⇒ Kinetic Gas Equation :-

The kinetic gas equation has been derived on the basis of postulates of the kinetic theory of gases. The eq<sup>n</sup> is :-

$$\left\{ PV = \frac{1}{3} m N u^2 \right\}$$

where,  $P$  = Pressure

$V$  = Volume

$m$  = Mass of a Gas molecule

$N$  = No. of molecules in Volume  $V$

$u$  = Root mean square velocity (rms)

### ⇒ Kinetic Energy of Gas molecules:-

The kinetic energy of gas molecules can be easily calculated on the basis of kinetic gas eq<sup>n</sup>.

Average K.E. of one molecule =  $\frac{1}{2} mu^2$

$$\text{K.E. of } N \text{ molecules} = \frac{1}{2} mNu^2 = \frac{3}{2} \times \frac{1}{3} mNu^2$$

$$= \frac{3}{2} PV = \frac{3}{2} RT \quad [ \because PV = \frac{1}{3} mNu^2 \text{ and } PV = RT \text{ for 1 mole of gas} ]$$

$\therefore R$  is constant

$\therefore$  KE of a gas  $\propto T$

Eg:- Calculate K.E. of 4g of  $N_2$  at  $-13^\circ C$

$$\text{soln} = E_K = \frac{3}{2} nRT = \frac{3}{2} \times \frac{4}{28} \times 8.314 \times 260 \\ = 463.21 \text{ J mol}^{-1}$$

## # Deviation from Ideal Gas Behaviour:-

A gas which obeys the gas laws and the gas eq<sup>n</sup>  $PV = nRT$  strictly at all temperatures and pressures is said to be an ideal gas. The molecules of ideal gases are assumed to very small with no attractive forces between one another. But no real gas strictly obeys the gas eq<sup>n</sup> at all temperatures and pressures.

Deriations from ideal behaviour are observed particularly at high pressures or low temperatures. The deviation from ideal behaviour is expressed by introducing a factor  $Z$  known as Compressibility factor in the ideal gas eq<sup>n</sup>.  $Z$  may be expressed as 
$$Z = \frac{PV}{nRT}$$

→ In case of ideal gas,  $PV = nRT$ .  $\therefore Z = 1$

→ In case of real gas,  $PV \neq nRT$   $\therefore Z \neq 1$

Thus, in case of real gases  $Z$  can be  $< 1$  or  $> 1$

(1) When  $Z < 1$ , it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour.

(2) When  $Z > 1$ , it is a positive deviation. It shows that the gas is less compressible than expected from ideal behaviour.

## $\Rightarrow$ Causes of deviation from ideal behaviour:-

The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases. There are:-

- (1) The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.
- (2) The forces of attraction between gas molecules are negligible.

The first assumption is valid only at low pressures and high temperature, when the volume occupied by the gas molecules is negligible as compared to the total volume of the gas. But, at low temperature and high pressure, the molecules being in compressible the volumes of molecules are no more negligible as compared to the total volume of the gas.

The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored.

## # Van Der Waal's Equation:

The general gas eq<sup>n</sup>  $PV = nRT$  is valid for ideal gases only. Van Der Waal in 1873 modified the gas eq<sup>n</sup> by introducing two correction terms, one for volume and the other for pressure to make the eq<sup>n</sup> applicable to real gases as well.

### → Volume Correction:-

Let the correction term be  $v$

$$\therefore \text{Ideal volume } v_i = (V - v)$$

$$\text{Now } v \propto n \text{ or } v = nb$$

( $n$  = no. of moles of real gas,  $b$  = constant of proportionality called Van der Waal's constant)

$$\therefore v_i = V - nb$$

$b = 4 \times$  volume of a single molecule.

### → Pressure Correction:-

Let the correction term be  $p$

$$\therefore \text{Ideal pressure } p_i = (P + p)$$

$$\text{Now, } P \propto \left(\frac{n}{V}\right)^2 = \frac{an^2}{V^2}$$

Where  $a$  is constant of proportionality called another Van der Waal's constant.

Hence, ideal pressure

$$P_i = \left( P + \frac{an^2}{V^2} \right)$$

Here,  $n$  = no. of moles of real gas

$V$  = Volume of the container

$a$  = A constant whose value depends upon the nature of the gas

Substituting the values of ideal volume and ideal pressure, the modified eq<sup>n</sup> is obtained as

$$\left( P = \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Eg:- 1 mole of  $SO_2$  occupies a volume of 350 ml at 300 K and 50 atm pressure. Calculate the Compressibility factor of the gas.

Sol:-  $P = 50 \text{ atm}$   $V = 350 \text{ ml} = 0.350 \text{ litre}$

$n = 1 \text{ mole}$

$$T = 300 \text{ K} \quad \therefore Z = \frac{PV}{nRT}$$

$$\therefore Z = \frac{50 \times 0.350}{1 \times 0.082 \times 300} = 0.71$$

Thus,  $SO_2$  is more compressible than expected from ideal behaviour

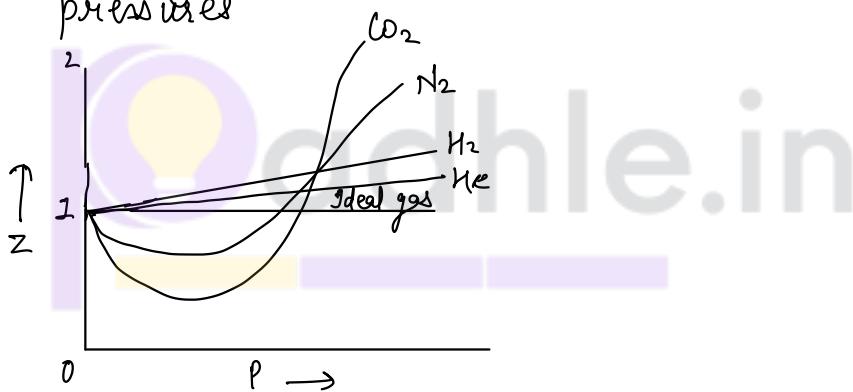
⇒ Vander Waal's Equation, different forms:-

→ At low pressures, ' $v$ ' is large and ' $b$ ' is negligible in comparison with  $V$ . The Vander Waal's eqn reduces to:-

$$\left( P + \frac{a}{V^2} \right) V = RT ; \quad PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V} \text{ or } PV < RT$$

This accounts for the dip in  $PV$  vs  $P$  isotherm at low pressures



Deviation of gases from ideal behaviour with pressure

⇒ At fairly high pressure

$\frac{a}{V^2}$  may be neglected in comparison with  $P$ .

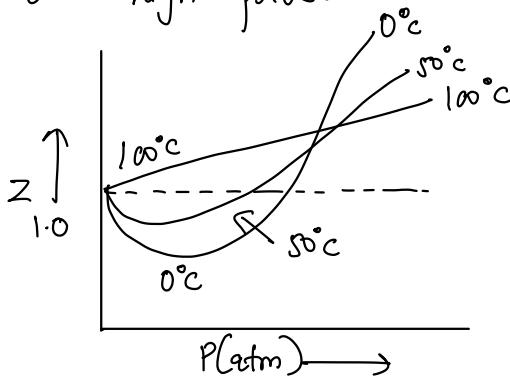
The Vander Waal's Eqn becomes

$$P(V-b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb \text{ or } PV > RT$$

This accounts for the rising parts of the PV vs P isotherm at high pressures



The plot of  $Z$  vs  $P$  for  $\text{N}_2$  gas at different temperature is shown here

→ At very low pressures:-  $V$  becomes so large that both  $b$  and  $\frac{a}{V^2}$  become negligible and the Vander Waals eqn reduces to  $PV = RT$ . This shows why gases approach ideal behaviour at very low pressures.

→ Hydrogen and Helium:- These are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extremely small.

So,  $\frac{a}{V^2}$  is negligible even at ordinary temperatures.

Thus  $PV > RT$ . Thus, Vander Waals eqn explains quantitatively the observed behaviour of real gases and so is an improvement over the ideal gas eqn. Vander Waals eqn accounts for the behaviour of real gases. At low pressures, the gas eqn can be written as:-

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

where, Z is known as compressibility factor. Its value at low pressure is less than 1 and it decreases with increase of  $P$ . For a given value of  $V_m$ ,  $Z$  has more value at higher temperature.

At high pressures, the gas eqn can be written as

$$P(V_m - b) = RT$$
$$Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$$

Here, the compressibility factor increases with increase of pressure at constant temperature and it decreases with increase of temperature at constant pressure. For the gases H<sub>2</sub> and He, the above behaviour is observed even at low pressures, since for these gases, the value of 'a' is extremely small.

Eg:- One litre of a gas at 300 atm and 473 K is compressed to a pressure of 600 atm and 273 K. The compressibility factors found are 1.072 and 1.375 respectively at initial and final states. Calculate the final volume.

$$\text{Soln:- } P_1 V_1 = Z n n R T_1 \quad \text{and} \quad P_2 V_2 = Z n n R T_2$$

$$\frac{P_2 V_2}{T_2} \times \frac{T_1}{P_1 V_1} = \frac{Z_2}{Z_1}$$

$$\text{or } V_2 = \frac{Z_2}{Z_1} \times \frac{T_2}{T_1} \times \frac{P_1 V_1}{P_2} = \frac{1.375}{1.072} \times \frac{273}{473} \times \frac{300 \times 1}{600} = 370.1 \text{ ml}$$

### ⇒ Boyle's Temperature ( $T_b$ )

Temperature at which real gas obeys the gas law over a wide range of pressure is called Boyle's temperature. Gases which are easily liquefied have a high Boyle's temperature [ $T_b(O_2) \approx 46 \text{ K}$ ] whereas the gases which are difficult to liquefy have a low Boyle's temperature [ $T_b(He) \approx 26 \text{ K}$ ].

$$\text{Boyle's temperature } T_b = \frac{q}{Rb} = \frac{1}{2} T_i$$

where,  $T_i$  is called Inversion temperature and  $q, b$ , are called van der Waals constant.

## # Critical Constants:-

⇒ Critical temperature ( $T_c$ ):- It ( $T_c$ ) is the maximum temperature at which a gas can be liquefied i.e. the temperature above which a gas can't exist as liquid.

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

⇒ Critical Pressure ( $P_c$ ):- It is the minimum pressure required to cause liquefaction at  $T_c$ .

$$\left[ P_c = \frac{a}{27b^2} \right]$$

⇒ Critical Volume: It is the volume occupied by one mol of a gas at  $T_c$  and  $P_c$   $V_c = 3b$

⇒ Molar heat Capacity of ideal gases:- Specific heat  $c$ , is defined as the amount of heat required to raise the temperature of 1 g of substance through 1 K, the unit of specific heat is calorie  $g^{-1} K^{-1}$  ( $\text{J cal}$ ) is defined as the amount of heat required to raise the temperature of 1 g of water through 1 K) Molar heat Capacity  $C$ , is defined as the amount of heat required to raise the temperature of 1 mole of a gas through 1 K.

Thus,

Molar heat Capacity = Specific heat  $\times$  molecular wgt. of the gas

For gases there are two values of molar heats, i.e., molar heat at constant pressure and molar heat at constant volume respectively denoted by  $C_p$  and  $C_v$ .  $C_p$  is greater than  $C_v$  and  $C_p - C_v = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$

From the ratio of  $C_p$  and  $C_v$ , we get the idea of atomicity of gas.

For monatomic gas  $C_p = 5 \text{ cal}$  and  $C_v = 3 \text{ cal}$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.67 \quad (\gamma \text{ is polytropic ratio} = \frac{C_p}{C_v})$$

for diatomic gas  $C_p = 7 \text{ cal}$  and  $C_v = 5 \text{ cal}$  in medium temperature range.

$$\gamma = \frac{7}{5} = 1.40$$

For polyatomic gas  $C_p = 8 \text{ cal}$  and  $C_v = 6 \text{ cal}$

$$\gamma = \frac{8}{6} = 1.33$$

also  $C_p = C_p \times m$ ,  $C_v = C_v \times m$

where,  $C_p$  and  $C_v$  are specific heat and  $m$ , is molecular weight.

Eg:- Calculate Vander Waals Constants for ethylene  
 $T_c = 282.8 \text{ K}$ ;  $P_c = 50 \text{ atm}$

$$\text{Sofn: } b = \frac{1}{8} \frac{RT_c}{P_c} = \frac{1}{8} \times \frac{0.082 \times 282.8}{50} = 0.057 \text{ liters/mole}$$

$$a = \frac{27}{64} R^2 \times \frac{T_c^2}{P_c} = \frac{27}{64} \times (0.082)^2 \times (282.8)^2 \times \frac{1}{50} = 4.47 \text{ liter}^2 \text{ atm mole}^{-2}$$

