

INTRODUCTION

Matter as we know broadly exists in three states. There are always two opposite tendencies between particles of matter which determine the state of matter

- Inter molecular attractive forces.
- The molecular motion / random motion.



In this chapter the properties and behaviour of the gases will be analysed and discussed in detail. These properties are measured with the help of the gas laws as proposed Boyle, Charles, Gay lussac etc

BOYLE'S LAW AND MEASUREMENT OF PRESSURE

Statement:

For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or

 $V \alpha \frac{1}{P}$

pressure of the gas.

this constant will be dependent on the amount of the gas and temperature of the gas.

$$P_1V_1 = P_2V_2$$



Application of Boyles Law : For the two parts 'A' and 'B' $P_1V_1 = K \& P_2V_2 = K$ hence it follows that $P_1V_1 = P_2V_2$.

Volume	Pressure :	Temperature		
Volume of the gas is the	Pressure = N/m^2 = Pa \rightarrow S.I. unit	Kelvin scale \rightarrow Boiling point = 373 K		
Volume of the container	C.G.S unit = $dyne-cm^2$	ice point = 273 K		
S.I. unit \rightarrow m ³	Convert 1N/m ² into dyne/cm ²	Fahrenheit scale \rightarrow B.P. = 212° F		
		ice point = 32° F		
C.G.S. unit \rightarrow cm ³	$\frac{1\text{N}}{1\text{m}^2} = \frac{10^5\text{dyne}}{10^4\text{cm}^2}$	Celcius scale \rightarrow B.P. = 100°C		
$1 \ \ell = 10^{-3} \ m^3$	$1 \text{N/m}^2 = 10 \text{ dyne/cm}^2$	ice point = 0°C		
$1 \ \ell = 10^3 \ \mathrm{cm}^9$				
$1 dm^3 = 1 \ \ell = 10^{-3} \ m^3$	$1 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2$	$\frac{C-0}{100-0} = \frac{K-273}{373-273} = \frac{F-32}{212-32}$		
$1 \text{ml} = 10^{-3} \ell = 1 \text{cm}^3$		$= \frac{R - R(0)}{R(100) - R(0)}$		
		where $R =$ Temp. on unknown scale.		

<u>Units</u>

Atmospheric pressure :

The pressure exerted by atmosphere on earth's surface at sea level is called 1 atm.

1 atm = 1.013 bar 1 atm= $1.013 \times 10^5 \text{ N/m}^2$ = 1.013 bar = 760 torr

Solved Examples

Ex.1 Arubber balloon contains some solid marbles each of volume 10 ml. A gas is filled in the balloon at a pressure of 2 atm and the total volume of the balloon is 1 litre in this condition. If the external pressure is increased to 4atm the volume of Balloon becomes 625 ml. Find the number of marbles present in the balloon.

Sol. Let the no. of marbles be = n.

volume of marble = 10 n ml. volume of balloon earlier = 1000 ml. later = 625 ml. Now for the gas inside the balloon temperature and amount of the gas is constant, hence boyles law can be applied

$$P_1V_1 = P_2V_2$$

$$4 \times (625 - 10n) = 2 \times (1000 - 10n)$$

$$625 \times 4 = 2000 - 20n + 40n$$

$$625 \times 4 - 2000 = 20n$$

$$\frac{625 \times 4 - 2000}{20} = n. \quad \frac{125}{5} = n \quad ; \qquad n = 25$$

MEASUREMENT OF PRESSURE

Barometer :

A barometer is an instrument that is used for the measurement of pressure. The construction of the barometer is as follows





Cross sectional view of the capillary column

A mercury barometer is used to measure atmospheric pressure by determining the height of a mercury column supported in a sealed glass tube. The downward pressure of the mercury in the column is exactly balanced by the outside atmospheric pressure that presses down on the mercury in the dish and pushes it up the column.



A thin narrow calibrated capillary tube is filled to the brim, with a liquid such as mercury, and is inverted into a trough filled with the same fluid.Now depending on the external atmospheric pressure, the level of the mercury inside the tube will adjust itself, the reading of which can be monitored. When the mercury column inside the capillary comes to rest, then the net forces on the column should be balanced. Applying force balance, we get,

$$P_{atm} \times A = m \times g$$

('A' is the cross-sectional area of the capillary tube) If ' ρ ' is the density of the fluid, then m = $\rho \times v$ hence, P_{atm} × A = ($\rho \times g \times h$) × A (v = A × h) ('h' is the height to which mercury has risen in the capillary)

or, $P_{atm} = \rho g h$

Normal atmospheric pressure which we call 1 atmosphere (1 atm), is defined as the pressure exerted by the atmosphere at mean sea level. It comes out to be 760 mm of Hg = 76 cm of Hg. (at mean sea level the reading shown by the barometer is 76 cm of Hg)

1 atm = $(13.6 \times 10^3) \times 9.8 \times 0.76$ = 1.013 × 10⁵ Pascal.

1 torr = 1 mm of Hg.

۲

1 bar = 10^5 N/m^2 (Pa)

Faulty Barometer : An ideal barometer will show a correct reading only if the space above the mercury column is vacuum, but in case if some gas column is trapped in the space above the mercury column, then the barometer is classified as a faulty barometer. The reading of such a barometer will be less than the true pressure.

For such a faulty barometer



Solved Examples

Ex.2 The reading of a faulty barometer is 700 mm of Hg. When actual pressure is 750 mm of Hg. The length of the air column trapped in this case is 10 cm. Find the actual value of the atmospheric pressure when reading of this barometer is 750 mm of Hg. Assume that the length of the Barometer tube above mercury surface in the container remains constant.

Sol.
$$P_0 = P_{gas} + 700 \rho g$$

 $\therefore P_{gas} = 750 \rho g - 700 \rho g = 50 \rho g$
 $\int_{\ell} \frac{100 \text{ mm}}{100 \text{ mm}}$

Now for the gas column in the capillary, amount and temperature are constant hence $P_1V_1 = P_2V_2$

$$(50 \text{ } \rho \text{g}) (100 \text{ A}) = \mathsf{P}'_{\mathsf{gas}} \times (50 \text{ A})$$

$$\therefore$$
 P'_{gas} = 100 ρg

Now, applying force balance in the new conditions :



 ${\sf P}_{\text{atm}}' = {\sf P}_{\text{gas}}' + 750 \ \rho g \!=\! 100 \ \rho g \!+\! 750 \ \rho g \!=\! 850 \ \rho g$

Hence, the atmospheric pressure is now, 850 cm of Hg.

Ex.3 In each of the following examples, find the pressure of the trapped gas.



Sol. Total pressure of gas column

$$= 75 + 10 = 85$$
 cm of Hg.

Ex.4

Ex.5

Sol. $P_{gas} = 65 \text{ cm of Hg.}$



 $P_{g} = 75 + 10 \cos \theta.$

Sol. From the above problem, it can be generalised that, applying force balance every single time is not necessary. If we are moving up in a fluid, then substract the vertical length, and while moving down add the vertical length.

CHARLES LAW

For a fixed amount of gas at constant pressure volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$$V \alpha T$$
 or $V = kT$

$$\frac{V}{T} = constant$$

where 'k' is a proportionality constant and is dependent on amount of gas and pressure.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Temperature on absolute scale, kelvin scale or ideal gas scale.

$$V = a + bt$$

Temperature on centigrade scale.



Relation: T = t + 273

- Since volume is proportional to absolute temperature. The volume of a gas should be theoretically zero at absolute zero temperature.
- Infact no substance exists as gas at a temperature near absolute zero, though the straight line plots can be extra plotted to zero volume. Absolute zero can never be attained practically though it can be approached only.
- By considering -273.15°C as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

Solved Examples

Ex.6 If the temp. of a particular amount of gas is increased from 27° C to 57° C, find final volume of the gas, if initial volume = 1 lt and assume pressure is constant.

Sol.
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

 $\frac{1}{(273+27)} = \frac{V_2}{(273+57)}$
So $V_2 = 1.1$ lt.

Ex.7 An open container of volume 3 litre contains air at 1 atmospheric pressure. The container is heated from initial temperature 27°C or 300 K to t°C or (t + 273) K the amount of the gas expelled from the container measured 1.45 litre at 17°C and 1 atm.Find temperature t.

Sol. : $T_{1}^{0} = 300 \text{ K}$

It can be assumed that the gas in the container was first heated to (t + 273), at which a volume ' ΔV ' escaped from the container

hence applying charles law :

$$\frac{3}{300} = \frac{3 + \Delta V}{t + 273}$$

Now, this volume ' Δ V' which escapes when the container get cooled

$$\therefore \quad \frac{\Delta V}{t+273} = \frac{1.45}{290}$$

Solve the two equations and get the value of ΔV and t.

determine ΔV & calculate t that will be the answer.

CALCULATION OF PAY LOAD

Pay load is defined as the maximum weight that can be lifted by a gas filled balloon.



For maximum weight that can be lifted, applying force balance

$$\begin{split} F_{buoyancy} &= M_{balloon} \times g + M_{pay \ load} \times g \\ \Rightarrow & \rho_{air} \ v.g. = \rho_{gas} \ v.g + Mg + mg. \\ mass of balloon = m & net \ force \ on \\ volume \ of balloon = v & balloon = 0 \\ density \ of \ air = \rho_{air} & (at \ equilibrium / when \\ balloon \ is \ incoming \\ density \ of \ gas \ inside \ the & with \ constant \ speed) \\ balloon = \rho_{oas} \end{split}$$

5

Solved Examples

Ex.8 A balloon of diameter 20 m weights 100 kg. Calculate its pay-load, if it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kg m⁻³.

 $[R = 0.0082 \text{ dm}^3 \text{ atm } \text{K}^{-1} \text{ mol}^{-1}]$

Sol. Weight of balloon = $100 \text{ kg} = 10 \times 10^4 \text{ g}$

Volume of balloon = $\frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{20}{2} \times 100\right)^3$

 $=4190 \times 10^{6} \text{ cm}^{3} = 4190 \times 10^{3} \text{ litre}$

Weight of gas (He) in balloon = $\frac{PVM}{RT}$

 $\left(\because PV = \frac{w}{M}RT \right)$

$$= \frac{1 \times 4190 \times 10^3 \times 4}{0.082 \times 300} = 68.13 \times 10^4 \text{ g}$$

 $\therefore \quad \text{Total weight of gas and balloon} \\ = 68.13 \times 10^4 + 10 \times 10^4 = 78.13 \times 10^4 \text{ g}$

Weight of air displaced = $\frac{1.2 \times 4190 \times 10^{6}}{10^{3}}$ $= 502.8 \times 10^{4} \text{ g}$

:. Pay load =
$$502.8 \times 10^4 - 78.13 \times 10^4$$

= **424.67** × **10**⁴ g

GAY-LUSSAC'S LAW

.'

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

 $P \alpha T$

 $\frac{P}{T}$ = constant \rightarrow dependent on amount and volume

of gas

 $\frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \text{temperature on absolute scale}$

originally, the law was developed on the centigrade scale, where it was found that pressure is a linear function of temperature $P = P_0 + bt$ where 'b' is a constant and P_0 is pressure at zero degree centigrade.



Example: $PV = K \implies V = K_1/p$

$$\frac{V}{T} = K_2 \implies V = K_2 T$$

$$\frac{K_1}{P} = K_2 T$$

$$PT = \frac{K_1}{K_2} = \text{const.} \implies P \alpha = \frac{1}{T} \implies ?$$
where are we wrong ?

This is wrong because we are varying temperature &

 $K_1 = f(1)$ thus K_1 will change according to temperature

So $\frac{K_1}{K_2}$ will be a function of temp & not constant.

Solved Examples

Ex.9 The temperature of a certain mass of a gas is doubled. If the initially the gas is at 1 atm pressure. Find the % increase in pressure ?

Sol.
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
; $\frac{1}{T} = \frac{P_2}{2T}$

% increase =
$$\frac{2-1}{1} \times 100 = 100\%$$

Ex.10 The temperature of a certain mass of a gas was increased from 27°C to 37°C at constant volume. What will be the pressure of the gas.

Sol.
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
; $\frac{P}{300} = \frac{P_2}{310}$; $P_2 = \frac{31}{30}P$

AVOGADRO'S HYPOTHESIS

For similar values of pressure & temperature equal number of molecules of different gases will occupy equal volume.

 $N_1 \longrightarrow V$

(volume of N_1 molecules at P & T of one gas) $N_1 \longrightarrow V$

(volume of N₁ molecules at P & T of second gas)

⇒ Molar volume & volume occupied by one mole of each and every gas under similar conditions will be equal.

One mole of any gas or a combination of gases occupies 22.413996 L of volume at STP.

The previous standard is still often used, and applies to all chemistry data more than decade old, in this definition **Standard Temperature and Pressure STP** denotes the same temperature of 0°C (273.15K), but a slightly higher pressure of 1 atm (101.325 kPa).

Standard Ambient Temperature and Pressure (SATP), conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e. exactly 10^5 Pa) At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol⁻¹ (Ref. NCERT)

EQUATION OF STATE

Combining all the gas relations in a single expression which discribes relationship between pressure, volume and temperature, of a given mass of gas we get an expression known as equation of state.

$$\frac{PV}{T} = constant$$

(dependent on amount of the gas (n)).

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

Ideal gas Equation :

$$\frac{PV}{nT} = constant \qquad [universal constant]$$

= R (ideal gas constant or universal gas constant)

$$R = 8.314 \text{ J/Kmole} \approx 25/3$$

= 1.987 cal/mole
$$\approx 2$$

= 0.08 Latm/K/mole $\approx 1/12$

Solved Examples

- **Ex.11** Some spherical balloons each of volume 2 litre are to be filled with hydrogen gas at one atm & 27° C from a cylinder of volume 4 litres. The pressure of the H₂ gas inside the cylinder is 20 atm at 127°C. Find number of balloons which can be filled using this cylinder. Assume that temperature of the cylinder is 27°C.
- Sol. No. of moles of gas taken initially

$$=\frac{20\times4}{R\times400}=2.43$$
 L

No. of moles of gas left in cylinder

$$=\frac{1\times4}{R\times300}=0.162L$$

No. of moles of gas to be filled in balloons

$$= 2.43 - 0.162 = 2.268$$

Let we have 'n' balloons that we can fill

No. of moles of gas that can be filled in 1 balloon

$$=\frac{1\times 2}{0.082\times 300}=0.081$$

 $\therefore 0.081 \times n = 2.268$

$$n = 28$$
 balloons.

DALTONS LAW OF PARTIAL PRESSURE

Partial pressure :

In a mixture of non reacting gases partial pressure of any component of gas is defined as pressure exerted by this component if whole of volume of mixture had been occupied by this component only.



Partial pressure of first component gas

$$P_1 = \frac{n_1 RT}{v}$$
; $P_2 = \frac{n_2 RT}{v}$; $P_3 = \frac{n_3 RT}{v}$

Total pressure = $P_1 + P_2 + P_3$.

Daltons law :

For a *non reacting* gaseous mixture total pressure of the mixture is the summation of partial pressure of the different component gases.

$$P_{Total} = P_1 + P_2 + P_3$$

= $\frac{(n_1 + n_2 + n_3)RT}{V}$
 $\frac{P_1}{P_T} = \frac{n_1}{n_T} = x_1$

(mole fraction of first component of gas)

$$\frac{\mathsf{P}_2}{\mathsf{P}_T} = \frac{\mathsf{n}_2}{\mathsf{n}_T} = \mathsf{x}_2$$

(mole fraction of second component of gas)

$$\frac{P_3}{P_T} = \frac{n_3}{n_T} = x_3$$

(mole fraction of third component of gas)

Solved Examples

- **Ex.12** The stop cock connecting the two bulbs of volume 5 litre and 10 litre containing as ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure if the temperature remains same.
- **Sol.** After the opening of the stop cock the pressure of the each bulb will remain same.

At the beginning, the no. of moles of gas in

$$A = \frac{10 \times 6}{RT}$$

At the beginning, the no. of moles of gas in



 \therefore total no. of moles at the beginning = $\frac{105}{RT}$

Total no. of moles of gas before opening the stop cock

= total no. of moles of gas after opening stop cock

$$=\frac{105}{RT}$$

 \therefore pressure after the opening of the stop cock

$$P = \frac{105}{RT} \ge \frac{RT}{V_{total}} = \frac{105}{10+5} = 7 \text{ atm}$$

- **Ex.13** A mixture of NO₂ & CO having total volume of 100 ml contains 70 ml of NO₂ at 1 atm, mixture is left for some time and same NO₂ get dimerised to N_2O_4 such that final volume of the mixture become 80 ml at 1 atm, calculate the mole fraction of NO₂ in final equilibrium mixture.
- Sol. Initial volume of $NO_2 = 70 \text{ ml}$ Initial volume of CO = 100 - 70 = 30 mlFinal volume of mixture = 80 ml Let the volume of NO_2 in final mixture be x Let 'v' ml NO_2 be converted to N_2O_4

$$2NO_2 \longrightarrow N_2O_4$$
$$V \quad V/2$$

Hence final volume

= volume of CO + volume of NO₂ left + volume of N_2O_4 formed

$$= 30 + 70 - V + V/2 = 80$$

V = 40 ml

Hence volume of NO₂ left = 70 - V = 30 ml Now as volume \propto moles

:. mole fraction = volume fraction = $\frac{30}{80} = \frac{3}{8}$

ANALYSIS OF GASEOUS MIXTURE

Vapour density :

Vapour density of any gas is defined as the density of any gas with respect to density of the H_2 gas under identical conditions of temperature T and pressure P.

vapour density = $\frac{\text{density of gas at T&P}}{\text{density of H}_2 \text{ under same P & T}}$

$$P = \frac{m}{V} \cdot \frac{RT}{M} \implies P = \rho \frac{RT}{M}$$
$$\implies \rho = \frac{PM}{RT}$$

vapour density = $\frac{PM_{gas}RT}{RT PM_{H_2}} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2}$

 $M_{gas} = 2 \times vapour density$

Average molecular mass of gaseous mixture :

total mass of the mixture divided by total no. of moles in the mixture

$$M_{\rm mix} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}}$$

If we have

 n_1' , n_2' and n_3' are moles of three different gases having of molar mass M_1' , M_2' and M_3' respectively.

$$M_{_{min}}=\,\frac{n_{1}M_{1}+n_{2}\,M_{2}+n_{3}\,M_{3}}{n_{1}+n_{2}+n_{3}}$$

Solved Examples

Ex.14 Calculate the mean molar mass of a mixture of gases having 7 g of Nitrogen, 22 g of CO_2 and 5.6 litres of CO at STP.

Sol. Moles of
$$N_2 = 7/28 = 1/4$$

Moles of
$$CO_2 = 22/44 = 1/2$$

Moles of
$$CO = 5.6 / 22.4 = 1/4$$

mean molar mass =
$$M_{min} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$

= (7+7+22)/1=36

GRAHAM'S LAW OF DIFFUSION/EFFUSION

Diffusion :

Net spontaneous flow of gaseous molecules from region of high concentration (higher partial pressure) to the region of lower concentration or lower partial pressure



rightarrow flow will be from both sides, N₂ will try to equalise its partial

pressure in both the vessels, and so will O₂.



Graham's Law :

"Under similar conditions of pressure (partial pressure) the rate of diffusion of different gases is inversely proportional to square root of the density of different gases."

• rate of diffusion $r \propto \frac{1}{\sqrt{d}}$

d = density of gas

$$\frac{r_{1}}{r_{2}} = \frac{\sqrt{d_{2}}}{\sqrt{d_{1}}} = \frac{\sqrt{M_{2}}}{\sqrt{M_{1}}} = \sqrt{\frac{V.D_{2}}{V.D_{1}}}$$

V.D is vapour density

$$r = volume flow rate = \frac{dV_{out}}{dt}$$

$$r = moles flow rate = \frac{dn_{out}}{dt}$$

r = distance travelled by gaseous molecules per

unit time =
$$\frac{dx}{dt}$$

 The general form of the grahams law of diffusion can be stated as follows, when one or all of the parameters are varied.

rate
$$\propto \frac{P}{\sqrt{TM}} A$$

P-Pressure, A-area of hole, T-Temp.,
M-mol. wt.

• If partial pressure of gases are not equal.

Then rate of diffusion is found to be proportional to partial pressure & inversely proportional to square root of molecular mass.

$$r \propto P$$

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

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

Selective diffusion :

If one or more than one components of a mixture are allowed to diffuse and others are not allowed then it is selective diffusion of those components.



 Platinum allows only H₂ gas to pass through Effusion : (forced diffusion) a gas is made to diffuse through a hole by the application of external pressure.



Solved Examples

Ex.15 In a tube of length 5 m having 2 identical holes at the opposite ends. $H_2 & O_2$ are made to effuse into the tube from opposite ends under identical conditions. Find the point where gases will meet for the first time.



- **Ex.16** Assume that you have a sample of hydrogen gas containing H_2 , HD and D_2 that you want to separate into pure components (H = ¹H and D = ²H). What are the relative rates of diffusion of the three molecules according to Graham's law?
- **Sol.** Since D_2 is the heaviest of the three molecules, it will diffuse most slowly, and let we call its relative rate 1.00. We can then compare HD and H₂ with D_2 .

Comparing HD with D₂, we have

 $\frac{\text{Rate of HD diffusion}}{\text{Rate of D}_2 \text{ diffusion}}$

$$= \sqrt{\frac{\text{Molecular mass of } D_2}{\text{Molecular mass of HD}}}$$
$$= \sqrt{\frac{4.0 \text{ amu}}{3.0 \text{ amu}}}$$
$$= 1.15$$

Comparing H₂ with D₂ we have

 $\frac{\text{Rate of H}_2 \text{ diffusion}}{\text{Rate of D}_2 \text{ diffusion}}$

$$=\sqrt{\frac{\text{Mass of } D_2}{\text{Mass of } H_2}} = \sqrt{\frac{4.0 \text{ amu}}{2.0 \text{ amu}}} = 1.41$$

Thus, the relative rates of diffusion are

 $H_2(1.41) > HD(1.15) > D_2(1.00).$

KINETIC THEORY OF GASES

Postulates / assumptions of KTG :

- A gas consists of tiny spherical particles called molecules of the gas which are identical in shape & size (mass)
- The volume occupied by the molecules is negligible in comparision to the total volume of the gas.

For an ideal gas, volume of the ideal gas molecule $\simeq 0$.

- Gaseous molecules are always in random motion and collide with other gaseous molecules & with the walls of the container.
- Pressure of the gas is due to these molecular collisions among themselves and with walls of the container
- These collisions are elastic in nature
- Molecular attraction forces are negligible. Infact, for an ideal gas attractive or repulsive forces are equal to zero.
- Newton's laws of motion are applicable on the motion of the gaseous molecules.
- Effect of gravity is negligible on molecular motion.
- The average K.E. of gaseous molecules is proportional to the absolute temperature of the gas.

 $\frac{1}{2}$ M ($\overline{u^2}$) α T (bar is for average)

Kinetic equation of gaseous state (expression for pressure of gas).



m = mass of one molecule

 $\vec{U} = U_x\hat{i} + U_y\hat{j} + U_z\hat{k}$

Consider collision with face ABCD

inital
$$\vec{P}_i = mU_x \hat{i}$$

final $\vec{P}_{f} = -mU_{x}\hat{i}$

change in momentum due to collision $= 2 U_x m$ time taken between two successive collision with

face ABCD =
$$t = \frac{2\ell}{U_x}$$

frequency of collisions (f) = $\frac{1}{t} = \frac{U_x}{2\ell}$

change in momentum in one sec. = force

$$= 2 \text{ m } \frac{\mathsf{U}_{\mathsf{x}} \times \mathsf{U}_{\mathsf{x}}}{2\ell} = \frac{\mathsf{m}\mathsf{U}_{\mathsf{x}}^2}{\ell}$$

force due to all the molecules

$$= \frac{m}{\ell} \ \{U_{x_1}^2 + U_{x_2}^2 + \dots + Ux_N^2\}$$

average value of $U_N^2 = \overline{U_N^2}$

_

$$=\frac{Ux_{1}^{2}+U_{x_{2}}^{2}+....U_{x_{N}}^{2}}{N}$$

 $F_x = \frac{M}{\ell} \{ N \ \overline{U_x^2} \}$

all the three directions are equal as the motion is totally random in all directions, hence

$$\overline{U_x^2} = \overline{U_y^2} = \overline{U_z^2}$$
$$\overline{U^2} = \overline{U_x^2} + \overline{U_y^2} + \overline{U_z^2}$$
$$= 3 \ \overline{U_x^2}$$

$$F_x = \frac{M}{\ell} \cdot N \frac{1}{3} \overline{U^2}$$

=

Pressure =
$$\frac{F_x}{\ell^2} = \frac{1}{3} \frac{N}{\ell^3} \overline{U^2}$$

The volume of the container 'V' = ℓ^3

$$\therefore$$
 PV = $\frac{1}{3}$ mN $\overline{U^2}$ Kinetic equation of gases

where $\overline{U^2}$ is mean square speed

root mean square speed =
$$U_{ms} = \sqrt{U^2}$$

$$= \sqrt{\left(\frac{U_1^2 + U_2^2 + U_3^2 + \dots + U_N^2}{N}\right)}$$

Verification of Gaseous Laws Using Kinetic Equation :

• From postulates; $PV = \frac{1}{3} mN \overline{U^2}$ $\frac{1}{2} m \overline{U^2} \propto T = \lambda T$

Where ' λ ' is a proportionality constant

$$PV = \frac{2}{3} \left(\frac{1}{2}m \overline{U^2}\right) N \qquad ;$$

$$PV = \frac{2}{3} \lambda NT (N = Total number of molecules)$$

- Boyle's Law : N : constant
 T : constant
 PV = constant
- Charles law : N : constant
 P : constant
 V ∝ T
- Kinetic energy of gaseous molecule

(translational K.E.)

To calculate λ we have to use ideal gas equation (experimental equation)

$$PV = nRT$$

Kinetic equation $PV = \frac{2}{3} \lambda nRT = \frac{2}{3} \lambda$ (nN_A)T (n = number of moles of gas)

on comparing $\lambda = \frac{3}{2} \times \frac{R}{N_A}$

 $\lambda = \frac{3}{2} \text{ K where } \text{K} = \frac{\text{R}}{\text{N}_{\text{A}}}$ = Boltzmann constant Average K.E. of molecules = $\frac{1}{2} \text{ m} \overline{\text{U}^2} = \lambda \text{ T}$ Average K.E. = $\frac{3}{2} \text{ K T}$

(only dependent on temperature not on nature of the gas.)

Average K.E. for one mole =
$$N_A \left(\frac{1}{2} m \overline{U^2}\right)$$

= $\frac{3}{2}$ K $N_A T = \frac{3}{2} RT$

• Root mean square speed :

$$U_{rms} = \sqrt{U^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{mN_A}}$$

Where m-mass of one molecule

• Dependent on nature of gas i.e mass of the gas

$$U_{\rm rms} = \sqrt{\frac{3RT}{M}}$$
 M = molar mass

• Average speed :

$$U_{av} = U_1 + U_2 + U_3 + \dots U_N$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{\pi m}}$$

K is Boltzmman constant

• Most probable speed :

The speed possessed by maximum number of molecules at the given temperature

$$U_{MPS} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2KT}{m}}$$



Solved Examples

Ex.17 In a container of capacity 1 litre there are 10^{23} molecules each of mass 10^{-22} gms. If root mean square speed is 10^5 cm/sec then calculate pressure of the gas.

Sol.
$$PV = \frac{1}{3} MN \overline{U^2}$$

 $P = ?$
 $V = 10^{-3} m^3$
 $m = 10^{-25} kg$
 $N = 10^{23}$
 $\sqrt{U^2} = 10^5 cm/sec = 10^3 m/sec$
 $\overline{U^2} = 10^6 m^2/sec^2$
 $P \times 10^{-3} = \frac{1}{3} \times 10^{-25} \times 10^{23} \times 10^{10}$
 $P = \frac{1}{3} \times 10^{-2} \times 10^6 \times 10^3$
 $P = \frac{1}{3} \times 10^7 pascals$

MAXWELL'S DISTRIBUTIONS OF MOLECULAR SPEEDS

Postulates/Assumptions of speed distributions

- It is based upon theory of probability.
- It gives the statistical averages of the speed of the whole collection of gas molecules.
- Speed of gaseous molecules of may vary from 0 to ∞. The maxwell distribution of speed can be plotted against fraction of molecules as follows.

fraction of molecule having particular speed



- The area under the curve will denote fraction of molecules having speeds between zero and infinity
- Total area under the curve will be constant and will be unity at all temperatures.
- Area under the curve between zero and u₁ will give fraction of molecules racing speed between 0 to u₁. This fraction is more at T₁ and is less at T₂.
- The peak corresponds to most probable speed.
- At higher temperature, fraction of molecules having speed less than a particular value decreases.
- For Gases with different molar masses will have following graph at a given temperature.



REAL GASES

- Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.
- Real gases deviates from ideal behaviour because
 - Real gas molecules have a finite volume. {since on liquefaction real gases occupy a finite volume}
 - Inter molecular attractive forces between real gas molecules is not zero.

{Real gases can be converted into liquid where as ideal gases cant be}

 Deviation of real gases from ideal behaviour can be measured by using compresibility factor: (Z)

$$Z = \frac{(PV)_{real}}{(PV)_{ideal}} \qquad (PV)_{ideal} = nRT$$

 $Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$, V_M is volume of one mole of gas or molar volume.

$$Z = \frac{V_{m}}{V_{m ideal}}$$



Variation of Z with pressure at constant temperature :



Variation of Z with pressure at different temperature (for a gas):



Conclusions :

Z = 1 for ideal gas;

- Z > 1 at all pressures for He/H₂
- Z < 1 at low pressure (for all other gases);
- Z > 1 at high pressure (for all other gases)

VANDER WAAL EQUATION

OF REAL GASES

The ideal gas equation does not consider the effect of attractive forces and molecular volume.

vander Waal's corrected the ideal gas equation by taking the effect of

(a) Molecular volume

(b) Molecular attraction

• Volume correction :

Ideal gas equation :

 $P_i V_i = nRT$; In the equation 'V_i' stands for the volume which is available for free movement of the molecules.

V_{ideal} = volume available for free movement of gaseous molecule

hence, $V_i = V - \{volume not available for free movement\}$ For an ideal gas

 $V_i = V \{V = volume of container\}$

but for a real gas

 $\boldsymbol{V}_{i} \neq \boldsymbol{V}$, as all the volume is not available for free movement

Molecules have finite volume :

Excluded volume per molecule = $\frac{1}{2} \left\{ \frac{4}{3} \pi (2r)^3 \right\}$

= Co-volume per molecule.

The volume that is not available for free movement is called excluded volume.

let us see, how this excluded volume is calculated.



Excluded volume (not available for free momement)

For above example, the entire shaded region is excluded, as its centre of mass cannot enter this region.

If both molecules were ideal, then they would not have experienced any excluded volume but not in the case, of real gas as the centre of mass of '2' cannot go further.

Hence for this pair of real gas molecules,

Excluded volume per molecule

$$= \frac{1}{2} \left\{ \frac{4}{3} \pi \left(2r \right)^3 \right\} = 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

= excluded volume per mole of gas (b)

$$= N_A 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

= $4 \times N_A \times Volume of individual molecule$

for n moles, excluded volume = nb

 $V_i = V - nb$ volume correction

 Pressure correction or effect of molecular attraction forces :



Molecule in the middle of container

Due to these attraction, speed during collisions will be reduced

Momentum will be less

Force applied will be less

Pressure will be less.

 $P_{ideal} = P + \{ correction term \}$

Correction term α no. of molecules attracting the colliding molecule \propto (n/v).

Correction term α density of molecules \propto (n/v).

no. of collision α density of molecules $\propto \left(\frac{n}{v}\right)$

net correction term $\propto \left(\frac{n}{v}\right) \left(\frac{n}{v}\right) = \frac{an^2}{v^2}$

'a' is constant of proportionality

and this is dependent on force of attraction

Stronger the force of attraction greater will be 'a' (Constant)

$$P_i = P + \frac{an^2}{v^2}$$

Vander waal's equation is

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

VERIFICATION OF VANDER WAAL'S EQUATIONS

Variation of Z with P for vander waals' equation at any temp.



Vander waal equation for 1 mole

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

• AT LOW PRESSURE (at separate temp.)

At low pressure V_m will be high.

Hence b can be neglected in comparision to V_m . but

 $\frac{a}{V_m^2}$ can't be neglected as pressure is low

Thus equation would be

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

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_mRT} = 1$$

$$Z = 1 - \frac{a}{V_mRT}$$

$$Z < 1$$

Real gas is easily compressible as compared to an ideal gas.

• AT HIGH PRESSURE (moderate temp.)

V_mwill be low

so b can't be neglected in comparision to V_m

but $\frac{a}{V_m^2}$ can be neglected as compared to much higher values of P.

Then vander Waals' equation will be

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

$$PV_m - Pb = RT$$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$Z = \frac{Pb}{RT} + 1 \quad (Z > 1)$$

If Z > 1, then gas is more difficult to compress as compared to an ideal gas.

At low pressure and very high temperature.
 V_m will be very large

hence 'b' can't be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large $PV_m = RT$ (ideal gas condition)

♦ For H₂ or He a ~ 0 because molecules are smaller in size or vander Wall's forces will be very weak, these are non polar so no dipoledipole interactions are present in the actions.

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

'a' factor depends on inter molecular attractive forces.

 \mathbf{O} 'a' factor for polar molecule > 'a' factor for non polar molecule.

Ar

Solved Examples

Ex.18 Arrange following in decreasing 'a' factor

 (H_2O, CO_2, Ar) $H_2O > CO_2 >$ polar

O For non polar molecules :

Greater the size or surface area, greater will be vander waals' forces, so greater will be 'a' constant.

Ex.19 Arrange following gases according to 'a'

He, Ar, Ne, Kr.

 $a_{Kr} > a_{Ar} > a_{Ne} > a_{He}$

• More 'a' factor means higher will be boiling point.

O liquification pressure :

Is the pressure required to convert gas into liquid.

for easy liquefaction $a\uparrow$ and $P\downarrow$

When Z < 1, $V_m < V_{m, ideal}$

 \Rightarrow easily liquifiable

$$Z > 1$$
, $V_m > V_{m ideal}$

 \Rightarrow more difficult to compress.

Ex.20 Arrange the following according to liquification pressure.

n-pentane; iso-pentane, neo pentane.

$$a_{n-pentene} > a_{iso-pentane} > a_{neo-pentane}$$

liquification pressure = LP

 $L_{P_{n-pentane}} < L_{P_{iso pentane}} < L_{P_{neo pentane}}$

• **b** is roughly related with size of the molecule. (Thumb rule)

$$b = N_A 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

- **Ex.21** Two vander waals gases have same value of b but different a values. Which of these would occupy greater volume under identical conditions ?
- **Sol.** If two gases have same value of 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume. This is because the gas with a larger value of 'a' will have larger force of attraction and hence lesser distance between its molecules.



VIRIAL EQUATION OF STATE

It is a generalised equation of gaseous state. All other equations can be written in the form of virial equation of state.

Z is expressed in power series expansion of P or

$$\left(\frac{1}{V_{m}}\right)$$

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots$$

B-second virial coefficient

C-third virial coefficient

D-fourth virial coefficient

Vander waals' equation in virial form :

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

$$P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

$$Z = \frac{PV_m}{RT} = \frac{V_m}{(V_m - b)} - \frac{a}{V_m RT}$$

$$= \frac{1}{(1 - b/V_m)} - \frac{a}{V_m RT}$$

$$\frac{1}{1 - x} = 1 + x + x^2 + x^3 + \dots$$

$$Z = \left(1 + \frac{b}{V_{m}} + \frac{b^{2}}{V_{m}^{2}} + \frac{b^{3}}{V_{m}^{3}} + \dots \right) - \frac{a}{V_{m} RT}$$
$$= 1 + \frac{1}{V_{m}} \left(b - \frac{a}{RT}\right) + \frac{b^{2}}{V_{m}^{2}} + \frac{b^{3}}{V_{m}^{3}} + \dots$$

comparing vander waals equation with virial equation

$$B = b - \frac{a}{RT} ,$$
$$C = b^2, D = b^3$$

at low pressure : V_m will be larger

hence
$$\frac{1}{V_m^2}$$
, $\frac{1}{V_m^3}$ can be neglected
 $Z = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT} \right)$
If $\left(b - \frac{a}{RT} \right) = 0$
 \Rightarrow at $T = \frac{a}{Rb}$; $Z = 1$

so at $T = \frac{a}{Rb}$, gas will behave as an ideal gas (or follows Boyles law)

But at constant temperature, ideal gas equation is obeying Boyles law as $T = \frac{a}{Rb}$, so the temperature is called Boyles' temp.

$$T_{B} = \frac{a}{Rb}$$

$$T_{1}$$

$$T_{2}$$

$$Z = 1 - \frac{a}{V_{m}RT}$$

$$T_{2}$$

for a single gas, if we have two graphs as above, we must conclude $T_2 < T_1$. At Boyles' temperature 'a/RT' factor is compensated by 'b' factor, so Z = 1.

CRITICAL CONSTANT OF A GAS

When pressure increases at constant temperature volume of gas decreases



 $AB \rightarrow gas$

 $BC \rightarrow vapour + liquid$

 $CD \rightarrow liquid$

critical point : At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that

density of liquid = density of vapour

T_c or critical temp :

Temperature above which a gas can not be liquified

P_C or critical pressure :

minimum pressure which must be applied at critical temperature to convert the gas into liquid.

V_C or critical volume :

volume occupied by one mole of gas at $T_c \& P_c$

Critical constant using vander waals' equations :

$$\left(\mathsf{P} + \frac{\mathsf{a}}{\mathsf{V}_{\mathsf{m}}^2}\right)(\mathsf{V}_{\mathsf{m}} - \mathsf{b}) = \mathsf{R}\mathsf{T}$$

$$(PV_m^2 + a) (V_m - b) = RT V_m^2$$

 $PV_m^3 + aV_m - PbV_m^2 - ab - RTV_m^2 = 0$

$$V_m^3 - V_m^2 \left(b + \frac{RT}{P}\right) + \frac{a}{P}V_m - \frac{ab}{P} = 0$$

Given equation is cubic, hence there will be three roots of equation at any temperature and pressure. At critical point, all three roots will coincide and will give single value of $V = V_C$

At critical point, Vander Waals' equation will be

$$V_{m}^{3} - V_{m}^{2} \left(b + \frac{RT_{C}}{P_{C}} \right) + \frac{a}{P_{C}} V_{m} - \frac{ab}{P_{C}} = 0$$
 ...(1)

But, at critical point, all three roots of the equation should be equal, hence equation should be :

$$V_{m}^{3} - 3V_{m}^{2}V_{C} + 3V_{m}V_{C}^{2} - V_{C}^{3} = 0$$
 ...(2)
comparing with equation (1)

$$b + \frac{RT_{C}}{P_{C}} = 3V_{C} \qquad \dots(i)$$

$$\frac{a}{P_{C}} = 3V_{C}^{2} \qquad \dots(ii)$$

$$\frac{ab}{P_{C}} = V_{C}^{3} \qquad \dots(iii)$$

$$V_{c} = 3b$$

$$P_{C} = \frac{a}{3V_{C}^{2}} \qquad On substituting value of V_{C}$$

$$P_{c} = \frac{a}{3 (3b)^{2}} = \frac{a}{27b^{2}}$$

by (i) $\frac{RT_{c}}{P_{c}} = 3 V_{c} - b = 9b - b = 8b$

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

1

At critical point, the slope of PV curve (slope of isotherm) will be zero

$$\left(\frac{\partial \mathsf{P}}{\partial \mathsf{V}_{\mathsf{m}}}\right)_{\mathsf{T}_{\mathsf{C}}} = 0 \qquad ...(i)$$

at all other point slope will be negative 0 (zero) is the maximum value of slope.

$$\frac{\partial}{\partial V_{m}} \left(\frac{\partial P}{\partial V_{m}} \right)_{T_{C}} = 0 \quad(ii)$$

{Mathematically such points are known as point of inflection (where first two differentiation becomes zero)}

using the two, T_c , P_c and V_c can be calculated

by
$$V_c$$
 T_c & P_c

By any two a can be calculated but a calculated by V_c and T_c and a calculated by T_c and P_c may differ as these values are practical values and V_c can't be accurately calculated. So when we have $V_c T_c \& P_c$ given, use $P_c \& T_c$ to deduce 'a' as they are more reliable.

REDUCED EQUATION OF STATE

Reduced Temp : Temperature in any state of gas with respect to critical temp of the gas

$$T_r = \frac{T}{T_C}$$

Reduced pressure :

$$P_r =$$

 $\frac{P}{P_{c}}$

Reduced volume: $V_r = \frac{V_m}{V_C}$

Vander waals' equation,

$$\left(\mathsf{P} + \frac{\mathsf{a}}{\mathsf{V}_{\mathsf{m}}^2}\right)(\mathsf{V}_{\mathsf{m}} - \mathsf{b}) = \mathsf{R}\mathsf{T}$$

Substitute values :

$$\left(\mathsf{P}_{\mathsf{r}}\,\mathsf{P}_{\mathsf{C}}\,+\frac{\mathsf{a}}{\mathsf{V}_{\mathsf{r}}^{2}\,\mathsf{V}_{\mathsf{C}}^{2}}\right)\,(\mathsf{V}_{\mathsf{r}}\,\mathsf{V}_{\mathsf{C}}\,-\,b)\,=\,\mathsf{R}\,\mathsf{T}_{\mathsf{r}}\,\mathsf{T}_{\mathsf{C}}$$

Substitute the value of $\rm P_{\rm C}\,T_{\rm C}$ and $\rm V_{\rm C}$

$$\left(\mathsf{P}_{\mathsf{r}} \frac{\mathsf{a}}{27\mathsf{b}^{2}} + \frac{\mathsf{a}}{\mathsf{V}_{\mathsf{r}}^{2} (3\mathsf{b})^{2}} \right) (3\mathsf{b} \,\mathsf{V}_{\mathsf{r}} - \mathsf{b}) = \mathsf{RTr} \,\frac{\mathsf{8a}}{27 \,\mathsf{Rb}}$$
$$\left(\frac{\mathsf{P}_{\mathsf{r}}}{3} + \frac{\mathsf{1}}{\mathsf{V}_{\mathsf{r}}} \right) (3 \,\mathsf{V}_{\mathsf{r}} - 1) = \frac{\mathsf{8RT}_{\mathsf{r}}}{3}$$
$$\left(\mathsf{P}_{\mathsf{r}} + \frac{\mathsf{3}}{\mathsf{V}_{\mathsf{r}}^{2}} \right) (3\mathsf{V}_{\mathsf{r}} - 1) = \mathsf{8T}_{\mathsf{r}}$$

(Reduced equation of state)

Above equation is independent from a, b and R, so will be followed by each and every gas, independent of its nature.

Solved Examples

Ex.22 The vander waals constant for HCI are a = 371.843 KPa.dm⁶ mol⁻² and b = 40.8 cm³ mol⁻¹ find the critical constant of this substance.

Solution : The critical pressure,

$$P_{\rm C} = \frac{a}{27b^2} = \frac{371.843 \times 10^3}{27 \times (40.8)^2 \times 10^{-6}}$$
$$= \frac{371.843 \times 10^9}{27 \times (40.8)^2} = 8.273 \text{ x } 10^6$$
$$P_{\rm C} = 8.273 \text{ MPa}$$

The critical pressure, $T_C = \frac{8a}{27Rb}$ R = 8.314 KPa dm³ K⁻¹ mol⁻¹ 8a 8×371.843

$$T_{C} = \frac{64}{27Rb} = \frac{6 \times 61 \times 10^{-3}}{8.314 \times 27 \times 40.8 \times 10^{-3}}$$

= 324.79 = 324.8 K
The critical volume, V_C = 3b = 3 x 40.8
= 122.4 cm³

Ex.23 The vander waals constant for gases A, B and C are as follows :

Gas	a/dm ⁶ KPa mol ⁻²	$b/dm^3 mol^{-1}$
А	405.3	0.027
В	1215.9	0.030
С	607.95	0.032

Which gas has

(i) Highest critical temperature

- (ii) The largest molecular volume
- (iii) Most ideal behaviour around STP?
- Sol. $T_C = \frac{8a}{27Rb}$ Since, R is constant, higher the value of a/b, higher will be critical temperature.

 $V_C = 3b$ and $V_C \propto V_m$ (for a particular gas) therefore higher the value of V_C , higher will be molar volume of the gas.

If the critical temperature is close to 273 K, gas will behave ideally around the STP. Let us illustrate the result in a tabular form.

Gas	a/dm ⁶ KPa mol ⁻²	b/dm ³ mol ⁻¹	T _C	V _C	a/b
А	405.3	0.027	534.97 K	0.081	1.501 x 10 ⁴
В	1215.9	0.030	1444.42 K	0.09	$4.053 \ge 10^4$
С	607.95	0.032	677.07 K	0.096	1.89 x 10 ⁴

(i) B gas has the largest critical temperature.

(ii) C gas has the largest molecular volume.

(iii) A gas has the most ideal behaviour around STP

VAPOUR PRESSURE OF A LIQUID (AQUEOUS TENSION OF WATER)



this h denotes vapour pressure of liquid = pressure exerted by vapours of liquid

Vapour pressure depends on

(a) Temperature (T $\uparrow \Rightarrow$ VP \uparrow)

(b) Nature of the liquid

Vapour pressure is independent of amount of liquid & surface area of liquid.

Vapour pressure of the liquid is independent of pressure of any gas in the container,

$$\mathbf{P}_{\text{total}} = \mathbf{P}_{\text{gas}} + \mathbf{P}_{\text{water vapour}}$$

Solved Examples

Ex.24 In a container of capacity 1 litre, air and some liquid water is present in equilibrium at total pressure of 200 mm of Hg. This container is connected to another one litre evacuated container. Find total pressure inside the container when equilibrium is again stablised (aqueous tension or vapour pressure at this temp. is 96 mm Hg).

Sol. Total pressure = 200 mm of Hg = $P_{gas} + P_{vapour water}$

$$\Rightarrow P_{gas} + 96 = 200$$

$$P_{gas} = 104 \text{ mm of Hg}$$
 Initially

when second container is connected

$$P_1 = 104 \text{ mm of Hg}$$
 $P_2 = ?$
 $V_1 = 1$ $V_2 = 2 \text{ litre}$

 $P_{1}V_{1} = P_{2}V_{2}$ $104 \times 1 = P_{2} \times 2$ $52 = P_{2}$ After equilibrium is established $P_{total} = 52 + 96 = P_{gas} + P_{water}$ = 148 mm of Hg at equilibrium.

EUDIOMETRY

The analysis of gaseous mixtures is called eudiometry. The gases are identified by absorbing them in specified and specific reagents.

SOME COMMON FACTS

- Liquids and solutions can absorb gases.
- If a hydrocarbon is burnt, gases liberated will be CO₂ & H₂O. [H₂O is seperated out by cooling the mixture & CO₂ by absorption by aqueous KOH]
- If organic compound contains S or P, then these are converted into SO₂ & P₄O₁₀ by burning the organic compound.
- If nitrogen is present, then it is converted into N₂.
 [The only exception : if organic compound contains NO, group then NO, is liberated]
- If mixture contains N₂ gas & this is exploded with O₂ gas, do not assume any oxide formation unless specified.
- Ozone is absorbed in turpentine oil and oxygen in alkaline pyragallol.

Solved Examples

Ex.25 Carbon dioxide gas (CO_2) measuring 1 litre is passed over heated coke the total volume of the gases coming out becomes 1.6 litre. Find % conversion of CO₂ into carbon monoxide.

Sol. $CO_2 + C \longrightarrow 2CO$ CO_2 CO1 0 at time t 1 - x 2xInitial volume = 1 litre final volume = 1.6 litre Final volume = (1 + x) litres 1 + x = 1.6 x = 0.6 x = 0.6 $\frac{0.6}{1} \times 10 = 60\%$ of CO_2 will be converted into CO

Ex.26 100 ml of hydrocarbon is mixed with excess of oxygen and exploded. On cooling, the mixture was reported to have a contraction of 250 ml. The remaining gas when passed through a solution of aqueous KOH, the mixture shows a further contraction of 300 ml. Find molecular formula of the hydrocarbon.

Sol. $C_x H_y + \left(x + \frac{Y}{4}\right) O_2 \longrightarrow x CO_2 + \frac{y}{2} H_2 O$ 100 ml $x 100 \frac{y}{2} 100.$

mixture contains CO_2 , H_2O & excess O_2 on cooling, H_2O is separated, volume of H_2O = 250 ml

 $\frac{y}{2} \times 100 = 250$; y = 5,

as KOH absorbs CO_2 , hence 300 ml contraction is because of CO_2 that has been absorbed.

Volume of $CO_2 = 100 \text{ x} = 300$; x = 3Empirical formula = C_3H_5 ; molecular formula = C_6H_{10} .

Note : If water is already condensed out then total contraction in reaction mixture = {volume of reactants} - {volume of products + volume of unused species excluding volume of H₂O}.

Ex.27 100 ml of an hydrocarbon is burnt in excess of oxygen in conditions so that water formed gets condensed out the total contraction in volume of reaction mixture was found to be 250 ml when the reaction mixture is further exposed to aqueous KOH a further contraction of 300 ml is observed find molecular formula of hydrocarbon.

Sol. Using balanced chemical equation

$$C_{x}H_{y} + \left(\frac{x+y}{4}\right)O_{2} \longrightarrow xCO_{2} + \frac{y}{2}H_{2}O$$

$$t = 0 \quad 100 \text{ ml} \quad V \qquad 0 \qquad 0$$

t 0 V - 100
$$\left(x + \frac{y}{4}\right)$$
 100 x ml $\frac{100 y}{2}$

volume remained

$$V-100 \left(x + \frac{y}{4} \right) + 100x + 50y$$

-100 - V = 250
-25y + 50y = 150
25y = 150
y = 6