

GASEOUS STATE

1. INTRODUCTION

A given substance may occur in solid, liquid or gaseous phase depending upon the relative value of two tendencies namely Mutual Attraction (MA) and Escaping Tendency (ET)

- (i) if MA is greater than ET then substance will occur in solid state
- (ii) if MA is slightly greater than ET then substance will occur in liquid state
- (iii) if MA is very much less than ET then substance will occur in gaseous state

Out of the three states of matter, we will study the gaseous state.

This state of matter is characterized by sensitivity of volume change with change of pressure and temperature. It is due to large distance between molecules as compared to their own dimensions.

Gaseous state can be defined as collection of molecule far apart and continuously in motion.

2. MEASURABLE PROPERTIES OF GASES

- 2.1 Mass :** The mass of gas is generally used in the form of number of moles which is related as

$$(i) \text{ no. of moles} = \frac{\text{wt. in gm}}{\text{molecular mass of gases}} \left(n = \frac{w}{M} \right)$$

Two other useful formulae to calculate number of moles of gas are –

$$(ii) \text{ number of moles} = \frac{\text{no. of molecules of given gas}}{\text{Avogadro's number of molecules}} \left(n = \frac{N}{N_A} \right)$$

$$(iii) \text{ no. of moles} = \frac{\text{volume of given gas in litres at STP}}{22.4 \text{ L}}$$

- 2.2 Volume :** Volume of gas is volume of the container in which it is present, i.e. space which the gas molecules can occupy.

Relation between different units of volume

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^3 \text{ litre} = 10^6 \text{ cm}^3 = 10^6 \text{ ml} = 10^9 \text{ mm}^3.$$

- 2.3 Temperature :** Degree of hotness or coldness of a body is measured by temperature

$$\frac{C}{100} = \frac{K - 273}{100} = \frac{F - 32}{180}$$

C – Celcius scale, K – Kelvin scale, F – Fahrenheit scale

Note : In all the problems of gaseous state (i.e. in all gas law equations), temperature must be expressed in kelvin scale. i.e., $t^\circ\text{C} + 273.15 = TK$

- 2.4 Pressure :** Pressure of gas is defined as the force exerted by the gas on the walls of its container. It is often assumed that pressure is isotropic, i.e. it is the same in all the tree directions.

Units and determination of pressure of gas :

- (a) In SI unit the unit of pressure is the pascal (N/m^2) instead, the unit bar, kPa or MPa is used, generally.

$$1 \text{ bar} = 10^5 \text{ N/m}^2 = 100 \text{ kN/m}^2 = 100 \text{ kPa}$$

- (b) Pressure is also stated in mm or cm of mercury.

$$1 \text{ atm} = 760 \text{ mm Hg} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ KN/m}^2 = 1.0332 \text{ Kgf/cm}^2$$

$$1 \text{ Pa} = 1 \text{ Nm}^{-2} = 1 \text{ Kgm}^{-1} \text{ S}^{-1}$$

$$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3 (\text{SI unit})$$

$$1 \text{ L atm} = 101.325 \text{ J}$$

$$1 \frac{\text{KN}}{\text{m}^2} = 1 \times 10^3 \frac{\text{N}}{\text{m}^2} = \frac{1 \times 10^3 \times \text{kg}}{9.8 \times 10^4 \text{ cm}^2} = \frac{1}{98} \text{ kgf/cm}^2$$

$$1 \text{ Torr} = \frac{1}{98} \text{ Pa} = 133.322 \text{ Pa}$$

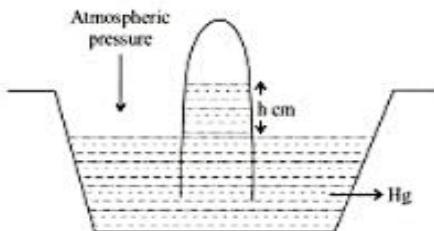
- (c) The pressure relative to the atmosphere is called gauge pressure. The pressure relative to the perfect vacuum is called absolute pressure.

$$\text{Absolute pressure} = \text{Gauge pressure} + \text{Atmosphere pressure}$$

- (d) Pressure is measured using a manometer which is a simple device with a horizontal arm and a U-tube carrying mercury or any other suitable liquid.

3. MEASUREMENT OF PRESSURE

- 3.1 Barometer :** The instrument used for the measurement of atmospheric pressure is called Barometer. It consists inverted a tube filled with mercury in a dish of mercury. The height of the mercury column is a measure of the atmospheric pressure at that place.



$$\text{vol. of Hg} = \text{Area} \times \text{Height} \\ = A \times h$$

$$\text{Mass of Hg} = \text{Volume} \times \text{Density} \\ A \times h \times d$$

$$\text{Force of mercury} = \text{Mass} \times g \\ = A \times h \times d \times g$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{A \times h \times d \times g}{A} = hdg$$

$$P = hdg$$

$$h = \frac{P}{dg}$$

$$P = 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pascal}$$

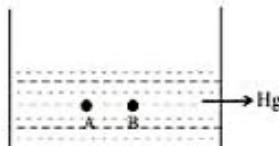
Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224311.jpg

$$d_{Hg} = 13.6 \text{ g/ml} = 13.6 \times 10^3 \text{ kg/m}^3$$

$$h = \frac{1.01325 \times 10^5}{13.6 \times 10^3 \times 9.8} = 0.76 \text{ m} = 760 \text{ cm} = 760 \text{ mm}$$

- Note :** 1. Pressure in liquid is independent on cross section area. It only dependent upon height of column.
 2. Pressure at all the points lying on the same horizontal level are always same.

$$P_A = P_B$$



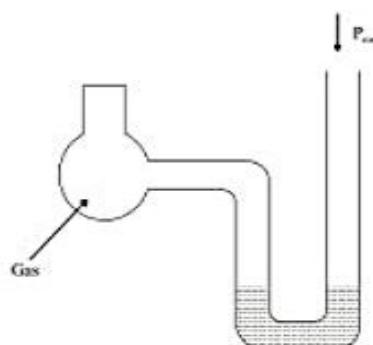
$$P_A - P_B = 0$$

3.2 Manometer : The instrument used for the measurement of the pressure of a gas called a manometer. It simply consists of a U shaped tube containing mercury usually. One limb of the tube is longer than the other. Two types of manometers are used. These are

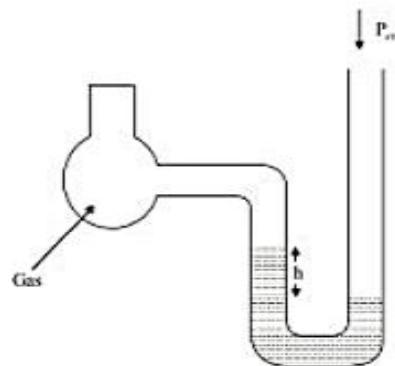
- (i) Open manometer - In this manometer the longer limb is open
- (ii) Closed manometer - In this manometer longer limb is closed

(I) Open manometer

(a) if level of Hg in the two limbs is same then $P_{gas} = P_{atm}$



(b) If level of Hg is shorter limb is higher than that of longer limb

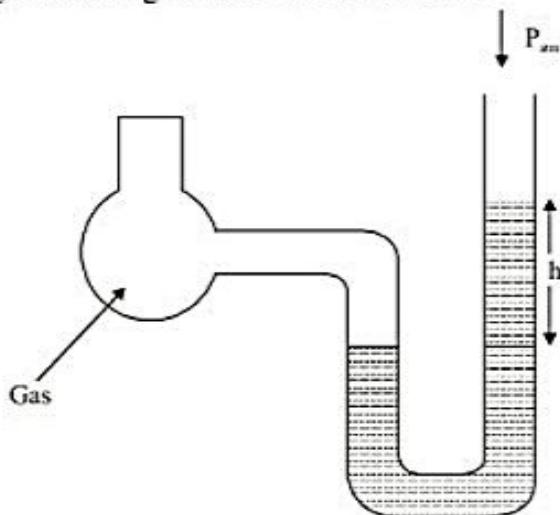


$$P_{atm} = P_{gas} + hdg$$

$$P_{gas} = P_{atm} - hdg$$

Saved /storage/emulated/0/Pictures/TouchShot/
 20170808_224312.jpg

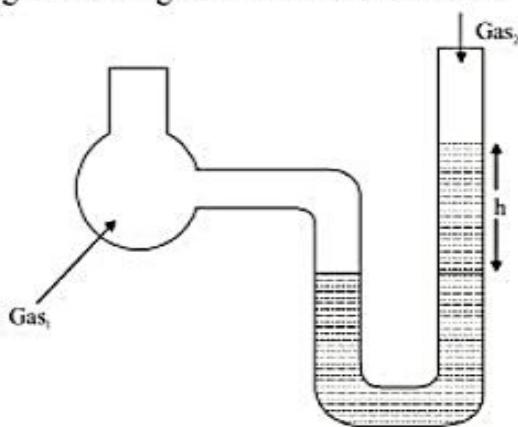
(c) If level of Hg in longer limb is higher than that of shorter limb



$$P_{\text{gas}} = P_{\text{atm}} + h \rho g$$

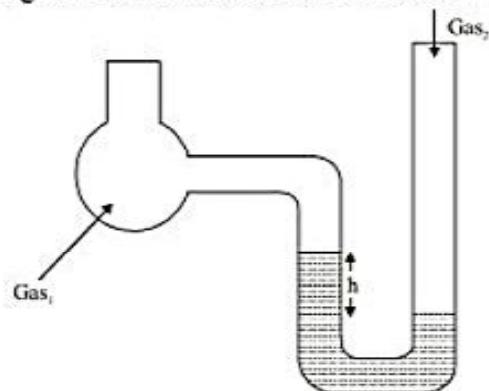
(ii) **Closed Manometer -**

(a) If level of mercury longer limb is higher than that of shorter limb



$$P_{\text{gas}_1} = P_{\text{gas}_2} + h \rho g$$

(b) If level of mercury in longer limb is lower than that of shorter limb.

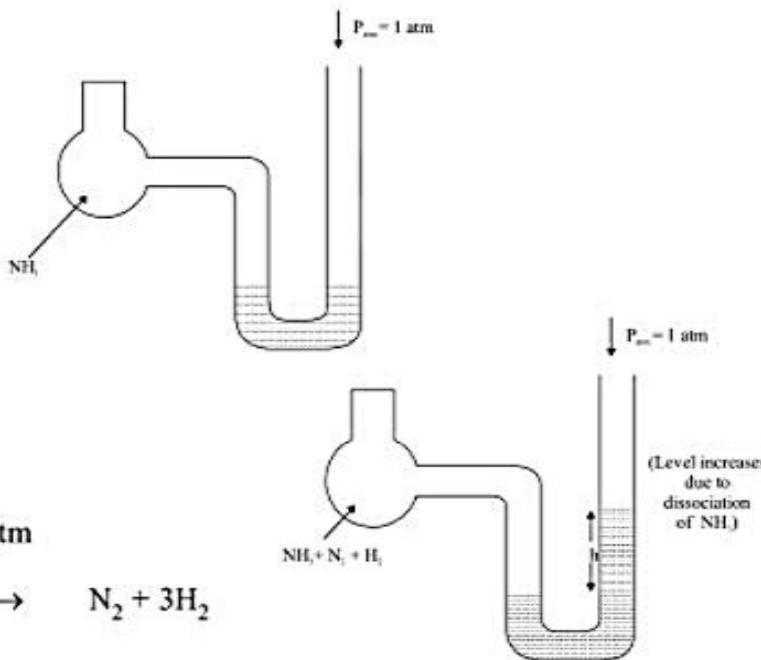


$$P_{\text{gas}_1} + h \rho g = P_{\text{gas}_2}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224312.jpg

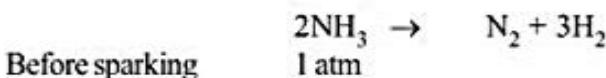
Illustration

1. A manometer attached to a flask contains NH_3 gas have no difference in Hg level initially as shown in diagram. After sparking into the flask there is difference of 19 cm in the mercury level in two column manometer. Calculate % dissociation of NH_3 .



Sol. $P_{\text{NH}_3} = 1 \text{ atm}$

$$P_{\text{NH}_3} + P_{\text{N}_2} + P_{\text{H}_2} = 1 + \frac{19}{76} = \frac{5}{4} \text{ atm}$$



After sparking	$(1 - P)$	$\frac{P}{2} \quad \frac{3P}{2}$
----------------	-----------	----------------------------------

$$P_{\text{final}} = 1 - P + \frac{P}{2} + \frac{3P}{2} = \frac{5}{4}$$

$$\text{or } P = \frac{1}{4}$$

$$\% \text{ dissociation} = \frac{1/4}{1} \times 100 = 25\%$$

Density :

Density may be defined as Mass per unit volume

$$d = \frac{m}{V}$$

Units :

CGS : g/cm³

MKS : kg/m³

Relation : $1 \text{ kg/m}^3 = 10^{-3} \text{ g/cm}^3$

Note : 1. Mass, volume and no. of moles are extensive properties (that depend on mass) hence additive in nature.

2. Density, Pressure and Temperature are intensive properties (they does not depend on mass) hence non-additive in nature.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224313.jpg

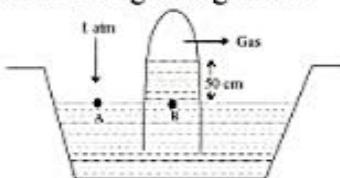
Illustration

1. In a barometric tube Hg is replaced by H_2O then find the height of H_2O column. Assume that vapour pressure of H_2O is negligible.

Sol. $h_1 d_1 g = h_2 d_2 g$ $[d_{Hg} = 13.6 \text{ g ml}^{-1}]$
 $h_1 d_1 = h_2 d_2$ $d_{H_2O} = 1 \text{ g ml}^{-1}]$
 $76 \times 13.6 = h_2 \times 1$
 $h_2 = 1033.6 \text{ cm}$ $= 10.336 \text{ m}$

Note : Density of Hg is high so column of small height is required.

2. Calculate the pressure of the gas in following arrangement



$$P_A = P_B$$

At the equilibrium position

$$P_{\text{atm}} = P_{\text{gas}} + P_{Hg}$$

$$76 \text{ cm} = P_{\text{gas}} + 50 \quad P_{\text{gas}} = 26 \text{ cm}$$

Exercise

An open tank is filled with Hg up to a height of 76 cm.

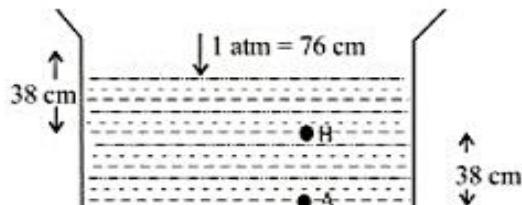
Find the pressure at the

(1) Bottom of the tank

(2) Mid of the tank

Atmospheric pressure = 1 atm

Ans. 2 atm, 1.5 atm

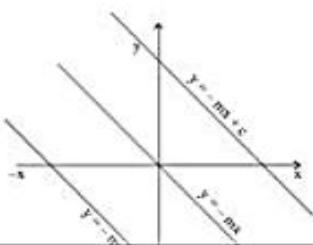
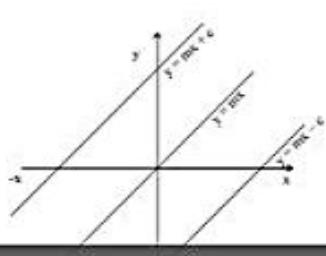
**4. GRAPHICAL ANALYSIS**

Four common equations and their graphical analysis

(1) Straight line equation

$$y = mx + c, \quad m = \text{slope} = \tan \theta, \quad c = \text{intercept}$$

If c is zero \Rightarrow straight line passing through origin.

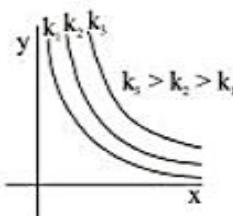
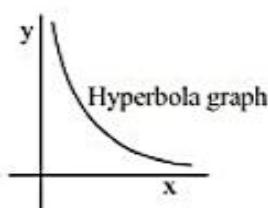
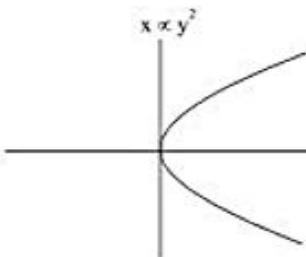
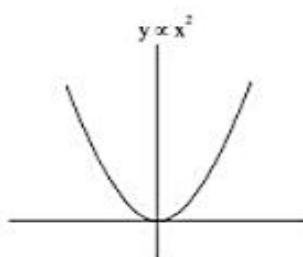
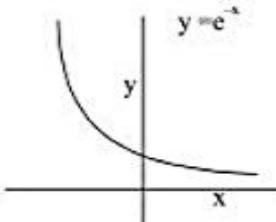
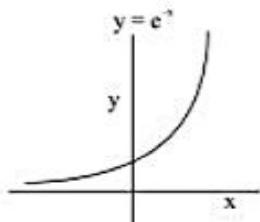


Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224313.jpg

(2) Hyperbola

$$yx = \text{constant } (k)$$

$$y = \frac{k}{x} \Rightarrow y \propto \frac{1}{x}$$

**(3) Parabola****(4) Exponential graph****5. GAS LAWS****5.1 Boyle's Law**

It relates the volume and the pressure of a given mass of a gas at constant temperature.

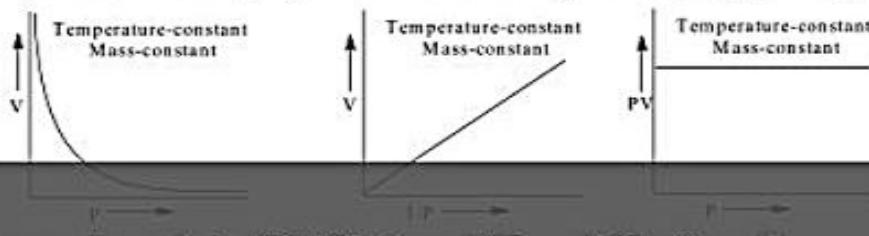
Boyle's law states that, "at constant temperature, the volume of a sample of a gas varies inversely with the pressure".

$$\therefore P \propto \frac{1}{V} \text{ (when temperature and number of moles are kept constant)}$$

The proportionality can be changed into an equality by introducing a constant k , i.e.,

$$P = \frac{k}{V} \text{ or } PV = k$$

Boyle's law can be verified by any one of the following three ways graphically.



Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224315.jpg

Alternatively, Boyle's law can also be stated as follows :

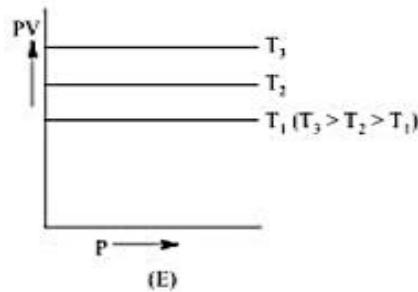
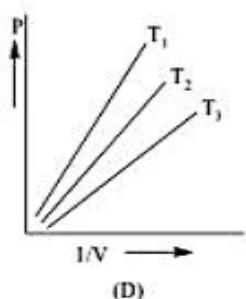
"Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant".

The value of the constant depends upon the amount of a gas and the temperature.

Mathematically, it can be written as,

$$P_1 V_1 = P_2 V_2 = P_3 V_3 = \dots$$

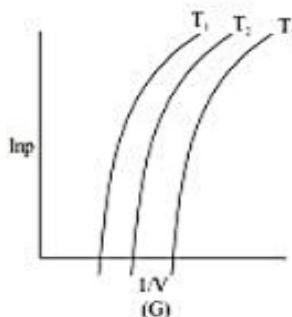
Location of straight line and curve changes with temperature in the **isotherm** shown in the following figure.



According to Boyle's law, $PV = \text{Constant}$ at constant temperature

$$\therefore \log P + \log V = \text{constant}$$

$$\log P = -\log V + \text{constant}$$



$$PV = k$$

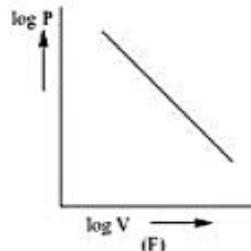
$$\ln P + \ln V = k'$$

$$\ln P = \ln V + k'$$

$$\ln P = -\ln V + k'$$

$$\ln P = \ln 1/V + k'$$

$$y = \ln x + c'$$



Illustration

1. A gas is present at a pressure of 2 atm. What should be the increase in pressure so that the volume of the gas can be decreased to $1/4^{\text{th}}$ of the initial value if the temperature is maintained constant.

Sol. $PV = \text{constant}$ for a given mass of gas at constant pressure

$$\Rightarrow P_1 V_1 = P_2 V_2 \quad P_1 = 2 \text{ atm} \quad V_1 = V \quad V_2 = V/4 \quad P_2 = ?$$

$$\text{Now, } 2 \times V = P_2 \times \frac{V}{4} \Rightarrow P_2 = 8 \text{ atm}$$

\therefore Pressure should be increased from 2 to 8 atm

\therefore total increase = $8 - 2 = 6$ atm.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224315.jpg

Exercise

1. A sample of gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmospheres? Assume that the temperature of the gas sample does not change.

Ans. 5 litre

5.2 Charle's law

It states "at constant pressure, the volume of a given mass of a gas, increases or decrease by $\frac{1}{273.15}$ th of its volume at 0°C for every rise or fall of one degree in temperature".

$$\frac{V_t}{V_0} = 1 + \frac{t}{273.15} \quad t \text{ (constant } n \text{ and } P)$$

$$\text{or } V_t = V_0 \left(1 + \frac{t}{273.15}\right) \quad \text{or } V_t = \frac{V_0(273.15 + t)}{273.15}$$

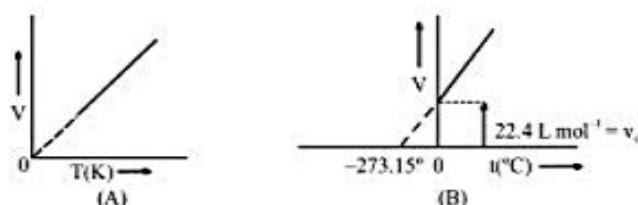
0°C on the Celsius scale is equal to 273.15 K at the Kelvin or absolute scale.
i.e. T_t (Temperature in Kelvin scale) = 273.15 + t

$$\therefore \text{From the above equation we get } \frac{V_t}{V_0} = \frac{T_t}{T_0} \quad \text{or} \quad \frac{V_t}{T_t} = \frac{V_0}{T_0}$$

i.e. The volume of a given gas is proportional to the absolute temperature.

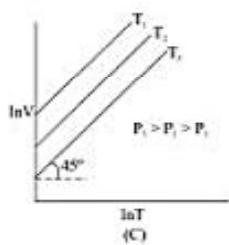
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{at constant } P)$$

- **Graphical representation :**



Graphs between V and T at constant pressure are called Isobars.

$\ln V$ vs $\ln T$



$$\frac{V}{T} = \text{constant (K)}$$

$$\begin{aligned} V &= KT \\ \ln V &= \ln K + \ln T \\ y &= C + mx \\ m &= 1 \end{aligned}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224316.jpg

Illustration

1. A gas occupies a volume of 580 ml at 17 °C. It is heated to 100 °C at constant pressure. Calculate the volume of the gas -

(A) 746 ml. (B) 760 ml. (C) 773 ml. (D) 780 ml.

Ans. A

Sol. Initial volume (V_1) = 580 ml,

$$T_1 = 17 + 273 = 290 \text{ K}$$

Final Volume (V_2) = ?

$$T_2 = 100 + 273 = 373 \text{ K}$$

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

$$\therefore V_2 = T_2 \times \frac{V_1}{T_1} = 373 \times \frac{580}{290} = 746 \text{ ml.}$$

Exercise

1. A gas occupies 3 litres at 32 °C and one atmospheric pressure. What volume will it occupy if the temperature is changed to 18 °C, the pressure remaining constant -

(A) 2.91 litres (B) 2.86 litres (C) 2.30 litres (D) None of these

Ans. B

5.3 Gay-Lussac's Law

(a) It states that at constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

(b) Mathematically - $P \propto T$ (at constant volume)

where P = pressure of gas

T = Absolute temperature

P = KT

or $\frac{P}{T} = K$

Hence, if the pressure of a gas is P_1 at temperature T_1 changes to P_2 at T_2 , volume remaining constant.

$$\text{then } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{constant}$$

$$\log P - \log T = \text{constant.}$$

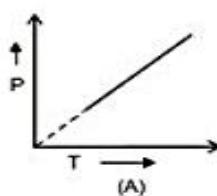
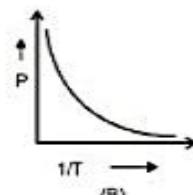
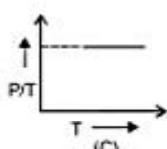
$$(c) P_1 = P_0 \left(1 + \frac{T}{273.15} \right)$$

where P_1 = Pressure of gas at t °C

P_0 = Pressure of gas at 0 °C

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224317.jpg

(d) Graphical representation -

(i) P vs T (ii) P vs $\frac{1}{T}$ (iii) $\frac{P}{T}$ vs T 

At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.

5.4 Avagadro's Law

(a) According to this law under the same condition of temperature and pressure, equal volumes of all gases contain equal no. of molecules.

$$V \propto n \text{ (At constant temperature & pressure)}$$

Where V = volume

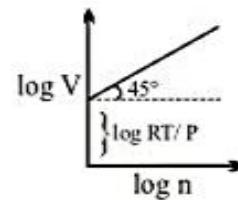
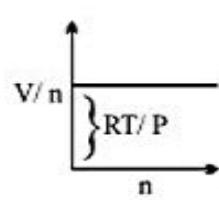
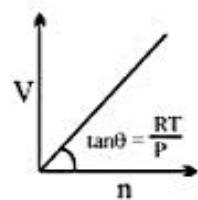
n = no of molecules

(b) Molar Volume or gram molecular volume is 22.4 litres or 22400 ml of every ideal gas at NTP is the volume occupied by its one gram mole and it is called molar volume or gram molecular volume.

(c) The mole Concept - Mole is defined as the total amount of substance that contains as many basic units as there are atoms in 12 g of the isotopes of carbon -12. Thus a mole will be defined as the Avogadro no of particles which is equal to 6.023×10^{23} .

(d) Loschmidt number - It the no of molecules present in the volume of a gas at S.T.P. Its value is 2.617×10^{19} per c.c.

Avogadro's law

 V vs n V/n vs n $\log V$ vs $\log n$ 

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224317.jpg

6. IDEAL GAS EQUATION

This equation is obtained by combining Boyle's, Charle's and Avogadro's law.

$$V \propto \frac{1}{P} \dots (i) \text{ (at constant temperature and definite mass)}$$

$$V \propto T \dots (ii) \text{ (at constant pressure and definite mass)}$$

$$V \propto n \dots (iii) \text{ (at constant temp and pressure)}$$

Combining eqs. (i), (ii) and (iii)

$$V \propto \frac{1}{P} \times T \times n$$

$$V = R \times \frac{1}{P} \times T \times n$$

$$PV = nRT \dots (1)$$

For 1 mole of the gas $n = 1$

$$PV = RT$$

$$\text{So } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \dots (2)$$

Where P_1, V_1, T_1 are the initial pressure, volume and temperature and P_2, V_2, T_2 are final values.
The above equation is called as ideal gas equation.

6.1 Ideal gas equation in terms of density

Let w and M be the mass and molecular mass of a gas; then

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

$$\text{Hence, eq. (1) becomes } PV = \frac{w}{M} RT$$

$$\text{or } P = \frac{w}{M} \cdot \frac{RT}{V} \quad \left[\frac{w}{V} = \frac{\text{mass}}{\text{Volume}} = \text{Density (d)} \right]$$

$$\text{or } P = \frac{d}{M} RT \dots (3)$$

Eq. (3) is modified form of gas equation. The above equations are strictly followed by ideal gases.

6.2 Natures of Molar Gas constant R

Gas equation for one mole of an ideal gas

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224318.jpg

$$PV = RT$$

or $R = \frac{P \times V}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{Length})^2}$$

$$\text{Volume} = (\text{Length})^3$$

So, $R = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{length})^3}{\text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{Temperature}} = \frac{\text{Work}}{\text{Temperature}}$

Thus, the value of the R should always be expressed in units of work per degree kelvin per mole.

6.3 Numerical values of R

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

One gram mole of a gas at one atmospheric pressure and 0°C (273 K) occupies a volume 22.4 litre.

$$P = 1 \text{ atmosphere},$$

$$T = 273 \text{ K},$$

$$V = 22.4 \text{ litre}$$

So, $R = \frac{1 \times 22.4}{273} = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$

If pressure is taken in dyne/cm² and volume in mL, $P = 76 \times 13.67 \times 981 \text{ dyne/cm}^2$, $V = 22400 \text{ mL}$ for 1 mole, $T = 273 \text{ K}$

So, $R = \frac{76 \times 13.67 \times 981 \times 22400}{273} = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$

Since, 1 joule = 10^7 erg, so

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

Since, 1 caloric = 4.184×10^7 erg, so

$$R = \frac{8.314 \times 10^7}{4.184 \times 10^7}$$

$$= 1.987 = 2 \text{ calorie K}^{-1} \text{ mol}^{-1}$$

Note : Although, R can be expressed in different unit, but for pressure-volume calculations, R must be taken in the same units of pressure and volume.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224318.jpg

Illustration

1. Pressure of gas contained in a closed vessel is increased by 0.4%, when heated by 1°C. Calculate its final temperature. Assume ideal nature.

Sol. Since no information is given about volume hence we can assume that volume is constant

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

$$\text{given } P_1 = P, \quad T_1 = T, \quad P_2 = P + \frac{0.04P}{100} = 1.004 P, \quad T_2 = T + 1$$

$$\therefore \frac{P}{T} = \frac{1.004P}{T+1} \Rightarrow T = 250 \text{ K}$$

$$\text{Final temp.} = 250 + 1 = 25 \text{ K}$$

2. An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant find

- (A) the air escaped out if vessel is heated to 900K.
 (B) temperature at which half of the air escapes out.

Sol. On heating a gas in a vessel, there are the number of moles of gas which go out, the volume of vessel remains constant.

Let initial no. of moles of gas at 300 K be 'n'. On heating 3/5 moles of air escape out at temperature T.

$$\therefore \text{Moles of air left at temperature } T = \left(n - \frac{3}{5} n \right) = \frac{2n}{5}$$

- (A) On heating vessel to 900 K, let n_1 moles be left,

$$n_1 T_1 = n_2 T_2 \Rightarrow n_1 \times 900 = 300 \times n \Rightarrow n_1 = \frac{1}{3} n$$

$$\therefore \text{moles escaped out} = n - \frac{n}{3} = \frac{2}{3} n \text{ moles}$$

- (B) Let $n/2$ moles escape out at temperature T, then

$$n_1 T_1 = n_2 T_2 \Rightarrow \frac{n}{2} \times T = n \times 300 \Rightarrow T = 600 \text{ K}$$

3. When 3.2 g of sulphur is vapourised at 450°C and 723 mm pressure, the vapours occupy a volume of 780 ml. What is the molecular formula of sulphur vapours under these conditions? Calculate the vapour density also.

$$\text{Sol. } PV = nRT \Rightarrow \frac{723}{760} \times \frac{780}{1000} = \frac{3.2}{M} \times 0.082 \times 723$$

$$M = 255.9$$

$$\text{no. of atoms of sulphur in one molecule} = \frac{M}{32} = 8$$

$$\therefore \text{Molecular formula of sulphur} = S_8$$

$$V. D. = \frac{M}{2} = \frac{255.9}{2} \Rightarrow 127.99$$

Exercise

5g of ethane is confined in a bulb of one litre capacity. The bulb is so weak that it will burst if the pressure exceeds 10 atm. At what temperature will the pressure of gas reach the bursting value?

Ans. 457.81°C

7. DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases."

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots \quad (\text{at constant } V \text{ and } T)$$

$$= \left(\frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + \dots \right) RT = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = \frac{nRT}{V}$$

where $n = n_1 + n_2 + n_3 + \dots$ = Total moles, V = Total volume

$$P_{\text{Total}} = \sum p_i = \frac{RT}{V} \sum n_i$$

If the two non-reacting gases A and B having n_A and n_B number of moles respectively are filled in a vessels of volume V at temperature T . Then

$$PV = (n_A + n_B)RT \quad \dots(1)$$

Partial pressure may be calculated as

$$p_A V = n_A RT$$

$$p_B V = n_B RT$$

$$\text{Total pressure } (p_A + p_B)V = (n_A + n_B)RT \quad \dots(2)$$

From (1) and (2)

$$P = p_A + p_B$$

$$\frac{p_A}{P} = \frac{n_A RT / V}{(n_A + n_B)RT / V} = \frac{n_A}{n_A + n_B} = x_A \quad (\text{mole fraction of A})$$

$$p_A = x_A \times P, \text{ similarly } p_B = x_B \times P$$

Partial pressure of a component = mole fraction \times total pressure.

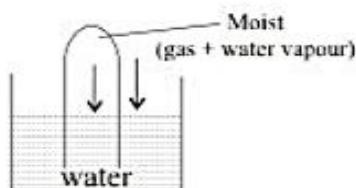
It has been observed that gases are generally collected over water and therefore are moist.

$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{water vapour}}$$

The pressure exerted by water vapour is constant with water at a particular temperature is called as aqueous tension, which varies directly with the temperature and becomes 760 mm at 100°C

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224319.jpg

$$\text{Relative Humidity (RH)} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$



Pressure of dry gas = Pressure of moist gas – aqueous tension.

Illustration

0.333 grams of alcohol displaced in a Victor Meyer apparatus 171 cm^3 of air measured over water at 15°C . The barometric pressure was 773 torr. Calculate the molecular weight of alcohol. (Aqueous tension at $15^\circ\text{C} = 13 \text{ torr}$.)

- (A) 33.34 g/mol. (B) 28.80 g/mol. (C) 46.0 g/mol. (D) 13.0 g/mol.

Ans. C

$$P_{\text{dry gas}} = 773 - 13 = 760 \text{ torr}$$

$$= \frac{760}{760} = 1 \text{ atm}$$

$$\therefore PV = nRT$$

$$1 \times \frac{171}{1000} = \frac{0.333}{\text{M.wt.}} \times 0.0821 \times 288$$

$$\text{M} = 46 \text{ g/mol}$$

Exercise

Atmospheric air contains 20% O_2 and 80% N_2 by volume and exerts a pressure of 760 mm. Calculate the partial pressure of each gas -

- | | |
|--------------------|--------------------|
| (A) 152 mm, 608 mm | (B) 608 mm, 152 mm |
| (C) 760 mm both | (D) None of these |

Ans. A

8. AMAGAT'S LAW OF PARTIAL VOLUME

According to this law at constant temperature and pressure, the total volume of non-reacting gaseous mixture is equal to the sum of partial volumes of each component gas present in mixture.

$$V_T = V_1 + V_2 + V_3 + \dots$$

Partial volume :

Partial volume of any component is defined as the volume occupied by that particular component measured under the given condition of pressure and temperature.

$$PV = nRT$$

$$V \propto n$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224320.jpg

Let us consider three non-reacting gases A, B and C are present in a container which have number of moles n_A , n_B and n_C respectively. For each gas partial volume is

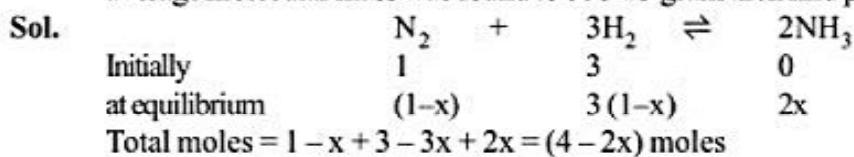
$$V_A = n_A \left(\frac{RT}{P} \right), \quad V_B = n_B \left(\frac{RT}{P} \right) \text{ and} \quad V_C = n_C \left(\frac{RT}{P} \right)$$

Total volume :

$$V_T = V_A + V_B + V_C = (n_A + n_B + n_C) \left(\frac{RT}{P} \right) = n_T \left(\frac{RT}{P} \right)$$

Illustration

1. 1 mole of N_2 and 3 moles of H_2 are mixed in 8.21 lit. container at 300 K to form NH_3 . If on equilibrium average molecular mass was found to be $\frac{34}{3}$ gram then find partial pressure of each component.



Given Average molecular mass = $\frac{34}{3}$

$$\frac{34}{3} = \frac{28(1-x) + 2(3-3x) + 17(2x)}{(4-2x)} \Rightarrow x = 1/2$$

So total number of moles = 3

$$PV = nRT \Rightarrow P = \frac{nRT}{V} = \frac{3 \times 0.0821 \times 300}{8.21} = 9 \text{ atm}$$

$$P_{N_2} = \frac{1-x}{3} \times P = \frac{0.5}{3} \times 9 = 1.5 \text{ atm}$$

$$P_{NH_3} = \frac{2x \times 9}{3} = \frac{2 \times 0.5 \times 9}{3} = 3$$

$$P_{H_2} = \frac{3-3x}{3} \times P = \frac{1.5}{3} \times 9 = 4.5 \text{ atm}$$

2. At constant temperature of 273 K, $\frac{1}{V}$ v/s P are plotted for 2 ideal gases A and B as shown. Find out the number of moles of gas A and B.

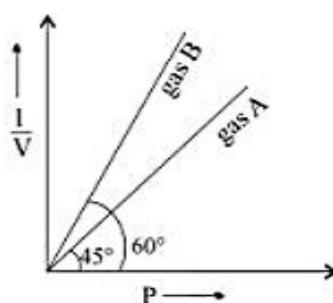
Sol. $PV = nRT, \quad P = \frac{1}{V} nRT$

$$\frac{1}{V} = \frac{1}{nRT} P$$

Comparing by equation :

$$y = mx + C$$

$$C = 0$$



$$m = \frac{1}{nRT} \quad (m = \tan \theta)$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224320.jpg

$$\tan \theta = \frac{1}{nRT} \quad n_A = \frac{1}{RT \tan \theta}$$

$$n_A = \frac{1}{0.0821 \times 273 \times \tan 45^\circ} \Rightarrow n_A = \frac{1}{22.4}$$

$$n_B = \frac{1}{RT \tan 60^\circ} = \frac{1}{22.4\sqrt{3}}$$

Exercise

1. A vessel of 2 lit. capacity contains hydrogen at 380 mm pressure at 27°C. 16 gm of O₂ is added to the container then find the total pressure ($R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$)

Ans. 6.65 atm

9. GRAHAM'S LAW OF DIFFUSION

Diffusion is the tendency of any substance to spread throughout the space available to it. Diffusion will take place in all direction and even against gravity.

Effusion is the process of gas molecular coming out of container through a small orifice, due to presence difference between container and surrounding atmosphere. The process of effusion is similar to diffusion and same formula are applicable with the only difference that effusion occurs due to presence difference. Effusion always followed by diffusion.

According to Graham, the rate of diffusion (or effusion) of a gas at constant pressure and temperature is inversely proportional to the square root of its molecular mass.

$$r \propto \sqrt{\frac{1}{M}}, \text{ at constant P and T}$$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}, \text{ at constant P and T}$$

Since molecular mass of gas = $2 \times$ vapour density, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$, at constant P and T

The rate of diffusion (or effusion) r of two gases under different pressure can be given by

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}} \text{ at constant T only.}$$

$$r = \frac{\text{Volume diffused (V)}}{\text{time taken}} = \frac{\text{moles diffused (n)}}{\text{time taken}}$$

distance travelled in a narrow tube of uniform cross-sectional area (x)
time taken

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224321.jpg

Therefore, according to Graham's law of diffusion (effusion) at constant P and T.

$$\frac{V_1 \times t_2}{t_1 \times V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

d_1 and d_2 are the respective densities and V_1 and V_2 are volumes diffused (effused) in time t_1 and t_2 .

$$\frac{n_1 \times t_2}{t_1 \times n_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where n_1, n_2 are moles diffused (effused) in time t_1 and t_2 .

$$\frac{x_1 \times t_2}{t_1 \times x_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where x_1 and x_2 are distances travelled by molecules in narrow tube in time t_1 and t_2 .

$$r = \frac{\text{moles diffused}}{\text{time taken}}$$

$$= \frac{\text{Distance travelled in a narrow tube}}{\text{time taken}}$$

$$= \frac{\text{pressure drop I}}{\text{pressure drop II}}$$

Note: It should be noted that the rate of diffusion or effusion actually depends on pressure difference of the gas and not simply on its pressure. Moreover the pressure difference is to be measured for this gas only i.e. if a container holds [He] at a pressure of 0.1 atm and if a small pin-hole is made in the container and if the container is placed in a room, then the rate of effusion of He gas from the container to outside depends only on its pressure difference, which is 0.1 atm (as there is no He in the atmosphere). This implies that the diffusion of a gas is not dependent on the diffusion of any other gas.

Whenever we consider the diffusion of gas under experimental conditions, we always assume that the gas diffuses in vacuum and during the time period for which the diffusion is studied the rate of diffusion (or the composition of diffusing or effusing mixture of gases) remains constant.

Application of graham's law of diffusion in enrichment of isotopes :

Enrichment of light component :

If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas

passing through will be enriched in lighter component by a factor $\sqrt{\frac{M_B}{M_A}}$, called enrichment factor

because lighter molecules effuse more rapidly than heavier ones. The remaining gas will be enriched in the heavier component.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224321.jpg

Each passage give an enrichment factor equal to $\sqrt{\frac{M_B}{M_A}}$ and so thousands of such barrier in succession are necessary to provide sufficient enrichment of heavier component.

Thus, enrichment factor for first barrier or operation $f_1 = \sqrt{\frac{M_B}{M_A}}$

$$\therefore \text{overall separation or enrichment factor } f = \frac{n'_A / n'_B}{n_A / n_B}$$

Where n_A, n_B and n'_A, n'_B are the concentration of two isotopically different components before and after processing. If required enrichment of gas A is attained in x -operation then,

$$(f_1)^x = \frac{n'_A / n'_B}{n_A / n_B} = f$$

$$\text{or } x \log f_1 = \log \left[\frac{n'_A / n'_B}{n_A / n_B} \right]$$

$$\text{or } x \log \left[\frac{M_B}{M_A} \right]^{1/2} = \log \left[\frac{n'_A / n'_B}{n_A / n_B} \right]$$

$$\text{or } \frac{x}{2} \log \left[\frac{M_B}{M_A} \right] = \log \left[\frac{n'_A / n'_B}{n_A / n_B} \right]$$

$$\text{or } x = \frac{2 \log \left(\frac{n'_A / n'_B}{n_A / n_B} \right)}{\log \left(\frac{M_B}{M_A} \right)}$$

Limitations

- (i) The laws of diffusion and effusion are applicable only when the pressure difference is very small.
- (ii) Correctly speaking the rate of diffusion and effusion are not constant throughout the time interval, but these rates may be assumed constant for a small time interval.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224322.jpg

Illustration

1. The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.
- Sol.** The molar ratio of oxygen and the other gas in the evacuated bulb = 1 : 1 and the total pressure of the gas mixture is 4000 mm, hence the partial pressure of each gas is 2000 mm.

The drop in the pressure of oxygen after 74 minutes

$$= \frac{(2000 - 1500) \times 74}{47} = 787.2 \text{ mm of Hg}$$

∴ After 74 minutes, the pressure of oxygen = 2000 - 787.2 = 1212.8 mm of Hg

Let the rate of diffusion of other gas be r_n , then $\frac{r_n}{r_{O_2}} = \sqrt{\frac{32}{79}}$

∴ Drop in pressure for the other gas = $787.2 \times \sqrt{\frac{32}{79}} = 501.01 \text{ mm of Hg}$

∴ Pressure of the other gas after 74 minutes = 2000 - 501.01 mm of Hg

$$\text{Molar ratio} = \frac{\text{Moles of unknown gas}}{\text{Moles of } O_2} = \frac{1498.99}{1212.8} = 1.236 : 1$$

2. Pure O_2 diffuses through an aperture in 224 seconds, whereas mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 sec under similar condition of pressure and temperature. What is molecular wt. of gas?

Sol. The gaseous mixture contains 80% O_2 and 20% gas.

$$\therefore \text{Average molecular weight of mixture } (M_{\text{mix}}) = \frac{32 \times 80 + 20 \times m_{\text{mix}}}{100} \quad \dots (\text{i})$$

Now for diffusion of gaseous mixture and pure O_2

$$\frac{r_{O_2}}{r_m} = \sqrt{\frac{M_{\text{mix}}}{M_{O_2}}} \text{ or } \frac{V_{O_2}}{V_{\text{mix}}} \times \frac{t_{\text{mix}}}{t_{O_2}} = \sqrt{\frac{M_{\text{mix}}}{32}}$$

$$\text{or } \frac{1}{224} \times \frac{234}{1} = \sqrt{\frac{M_{\text{mix}}}{32}} \quad \dots (\text{ii})$$

$$\therefore M_{\text{mix}} = 34.92$$

By (i) and (ii) mol weight of gas (m) = 46.6.

Exercise

Calculate the relative rates of diffusion of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ in the gaseous state (Atomic mass of F = 19).

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224323.jpg

10. CONNECTING CONTAINERS

- (1) When we are connecting two or more containers then the movement of any component of gas occurs in other container till the final pressure of the component in all the container become equal (that means partial pressure becomes equal)
- (2) To calculate composition of gaseous mixture in any container, we will use diffusion.

Illustration

1. A 10 litre container of 1 mole of gas at 300 K. It is connected to another container having volume 40 litre and is initially at 300K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate
 - (a) Moles and pressure of gas in both the containers before heating.
 - (b) Moles and pressure in two containers after heating. (Assume that initially the larger, container is completely evacuated)

Sol. (a) Before heating :

$$PV = nRT$$

$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

$$X = 0.8 \text{ moles}$$

$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$

(b) After heating :

$$\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$$

$$x_1 = 0.67 \text{ moles, Given } T_1 = 600 \text{ K}$$

$$\text{Pressure} = \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times 0.0821 \times 600}{40} = 0.821 \text{ atm}$$

Exercise

1. A mixture containing 1.12 litre D_2 and 2.24 litre of H_2 at NTP is taken inside a bulb connected to another bulb through a stop cock with a small opening. The second bulb is fully evacuated. The stop cock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of D_2 . Determine the % by weight of the gases in second bulb.

Sol. 41.66 %, 58.33%

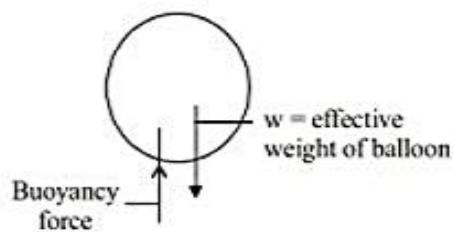
11. PAYLOAD OF BALLOON

Payload of a balloon is defined as maximum weight which a balloon can carry with it upward direction.
 $V = \text{Volume of Balloon}$, $d_a = \text{density of outside air}$

Saved /storage/emulated/0/Pictures/TouchShot/
 20170808_224323.jpg

d_{in} = density of gas inside, m = mass of balloon

$$\text{Payload} = d_{out} \times V \times g - [d_{in} V \times g + mg] \\ = [\text{Buoyancy force}] - [\text{effective wt. of balloon}]$$



Illustration

1. Calculate the payload of balloon of diameter 20 meter & weight 100 kg. If it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kgm⁻³. [R = 0.82 dm³ atm K⁻¹ mol⁻¹]

Sol. Weight of balloon = 100 kg = 10×10^4 g

$$\text{Volume of balloon} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{20}{2} \times 100 \right)^3 \\ = 4190 \times 106 \text{ cm}^3 = 4190 \times 10^3 \text{ litre}$$

$$\text{weight of gas (He) in balloon} = \frac{PV}{RT} = \frac{1 \times 4190 \times 10^3 \times 4}{0.082 \times 300} = 68.13 \times 10^4 \text{ g}$$

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

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

$$\therefore \text{Payload} = \text{wt. of air displaced} - (\text{wt. of balloon} + \text{wt. of gas})$$

$$\therefore \text{Payload} = 502.8 \times 10^4 - 7813 \times 10^4 = 424 \times 10^4 \text{ g} = 4.2467 \times 10^6 \text{ g}$$

Exercise

1. Calculate payload of a balloon having volume 100 litre. It is filled with helium gas at 0.2486 atm pressure and 300K. Density of air is 1.3 gm/litre and mass of material of balloon is 20 gm.

Ans. 1060

12. KINETIC THEORY OF GASES

The theoretical model for all the experimental gas laws can be analyse with the help of kinetic theory of gases which is based on following assumptions :

- (a) All the gases consists of very small molecules or atoms whose volume is negligible compared to volume of container
- (b) There is no interaction between gaseous particles (the interaction may appreciable affected under certain conditions of temperature and pressure).
- (c) The gaseous molecules are under a state of continuous motion which is unaffected by gravity (the random straight line motion is known as brownian motion)
- (d) Due to the continuous motion, collision between gaseous molecules with the wall of container occurs.

The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224325.jpg

- (e) The molecule moves with different speed.
- (f) All the collision occurring are considered to be perfectly elastic which implies that there is no loss of energy.
- (g) The average kinetic energy of gas will depends on absolute temperature only.

12.1 Equation for kinetic molecular theory

Pressure due to collisions of N_0 molecules on six faces of a cube = $\frac{1}{3} mN_0 U^2$

$$PV = \frac{1}{3} mN_0 U^2 = \frac{1}{3} MU^2$$

mN_0 = M (molar mass)

N_0 = Avogadro's number

U = root mean square velocity (U_{rms})

- Translation kinetic energy of n mole

$$\frac{1}{2} Mu^2 = \frac{3}{2} PV = \frac{3}{2} nRT$$

- Average translational kinetic energy per molecule

$$= \frac{3 RT}{2 N_0} = \frac{3}{2} KT$$

Where $K\left(\frac{R}{N_0}\right)$ is called Boltzmann's constant.

Its numerical value is 1.38×10^{-16} erg K⁻¹ molecule⁻¹

Thus average K.E. is proportional to absolute temperature.

If T = 0 K (i.e., -273.15°C), then average KE = 0

Thus absolute zero (0 K) is the temperature at which molecular motion ceases.

Illustration

1. Calculate the translational kinetic energy for one mole and one molecule of a gas at 300 K.

Sol. Translational kinetic energy per mole = $3/2 RT = 3/2 \times 8.314 \times 300 = 3741.3$ J/mole

Translational kinetic energy per molecule = $3/2 KT = 3/2 \times 1.38 \times 10^{-23} = 6.21 \times 10^{-21}$

Exercise

1. Calculate the translational kinetic energy for one mole and one molecule of a O₂ at 227°C.

Ans. 6235.5 J/mole, 1.035×10^{-20}

12.2 Different types of molecular velocities

- (i) **Root mean square velocity (U_{rms})**: It is defined as the square root of the mean of the squares of the velocities possessed by all the molecules present in the given sample of gas

$$U_{rms} = \sqrt{\frac{U_1^2 + U_2^2 + \dots + U_N^2}{N}}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224325.jpg

$$\therefore U_{\text{rms}} (\text{root mean square velocity}) = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

Where d is the density.

If N_1 molecules have velocity u_1 and N_2 molecules have velocity u_2 , then

$$U_{\text{rms}} = \sqrt{\frac{N_1 u_1^2 + N_2 u_2^2}{N_1 + N_2}}$$

- (ii) **Average velocity (U_{av})**: It is given by the arithmetic mean of square of the different velocities possessed by the molecules of the gases at a particular temperature.

$$U_{\text{av}} = \frac{U_1 + U_2 + \dots + U_n}{n}$$

$$U_{\text{av}} (\text{average velocity}) = \sqrt{\frac{8RT}{\pi M}}$$

- (iii) **Most probable velocity (U_{mp})**: It is defined as the velocity possessed by the maximum number of molecules of a gas at a given temperature.

$$U_{\text{mp}} (\text{most probable velocity}) = \sqrt{\frac{2RT}{M}}$$

If P and T both are given, use equation in terms of temperature i.e. use

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \text{ and not } \sqrt{\frac{3PV}{M}}$$

To have velocity in ms^{-1} (MKS) take $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, M in kg.

If density is in kg m^{-3} and P in N m^{-2} , velocity will be in ms^{-1}

Relation between rms velocity, average velocity and most probable velocity.

$$U_{\text{rms}} : U_{\text{av}} : U_{\text{mp}} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.2248 : 1.1284 : 1$$

$$U_{\text{rms}} = 1.2248 U_{\text{mp}}$$

$$U_{\text{av}} = 1.1284 U_{\text{mp}}$$

$$U_{\text{mp}} = 1.0854 U_{\text{av}}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224326.jpg

Illustration

Calculate U_{rms} , U_{av} , U_{mp} at 400 K for hydrogen molecule.

Sol. $U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 400}{2 \times 10^{-3}}} = 1823.6 \text{ m/s}$

$$U_{av} = 1.128 U_{mp} = 2057.8 \text{ m/s}$$

$$U_{rms} = 1.2248 U_{mp} = 2233.5 \text{ m/s}$$

Exercise

Calculate U_{rms} , U_{av} , U_{mp} at 600 K for oxygen molecule.

Ans. $U_{mp} = 558.4 \text{ m/s}$
 $U_{av} = 630.0 \text{ m/s}$
 $U_{rms} = 683.9 \text{ m/s}$

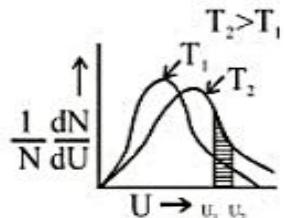
13. MAXWELL DISTRIBUTION OF MOLECULAR SPEED

- (a) The speed of a molecule of a gas changes continuously as a result of collisions with other molecules and with the walls of the container. Thus the net result is that we cannot speak of the speed of individual molecule; hence must consider the statistical averages of the speeds of the whole collection of gas molecules.
- (b) The manner in which the molecules of a gas are distributed over the possible speed ranges, from zero to very high values, was first investigated by Maxwell using the theory of probability. His results are expressed as the law of distribution of molecular speeds, one form of which is

$$dN = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mU^2}{2kT}}$$

- (c) The above expression gives the no. of molecules dN having speeds between U and $U + dU$ in terms of total no. of molecules N , present in the gas. m is mass of single gas molecule and T is the absolute temperature of gas.
- (d) The Maxwell distribution of speeds is customarily plotted with the fraction $\frac{1}{N} \left(\frac{dN_U}{dU} \right)$ as the ordinate and U as the abscissa.

$$\frac{1}{N} \frac{dN}{dU} = \frac{1}{dU} \left(\frac{dN}{N} \right)$$



Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224326.jpg

So, the term, $\frac{1}{N} \frac{dN}{dU}$ represents the fraction of molecules in the speed of u to $u + du$ per unit interval of speed. Roughly speaking, this gives the probability of finding a molecule with a speed between u and $(u + du)$. The distribution of two temperatures is shown in the fig.

- (e) The curve at any temperature is parabolic near the origin, since the factor u^2 is dominant in this region, the exponential function being approximately equal to unity. At high values of u , however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed (U_{mps}). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.
- (f) It can be seen from the given figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers. The total area under the curve gives the total no. of molecules in the collection, i.e. the no. of molecules comprising of all speeds. The area under the curve between any two speeds, for example, U_1 and U_2 , gives the total no. of molecules having speed between these two values.
- (g) The given figure illustrates the distribution of speeds at two temperatures T_1 and T_2 . Since the total no. of molecules is the same at both temperatures, increases the K.E. of the molecules, it follows that fraction of molecules having lower speed range decreases on decreasing the temperature whereas fraction of molecules having higher speed range increases on increasing the temperature.
- (h) Also the curve at the higher temperature T_2 has its U_{mps} shifted to a higher value compared with that for T_1 , whereas corresponding fraction molecules has decreased. But at the same time, the curve near U_{mps} has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

Illustration

1. For a sample containing O_2 and SO_2 mark out the **incorrect** statement
 - (A) At same temperature average speed of O_2 is greater than that of SO_2 ,
 - (B) If absolute temperature of O_2 is half to that of SO_2 gas than the speed distribution curves will be different.
 - (C) At same temperature & at lower speed, fraction of molecules of SO_2 will be greater.
 - (D) At same temperature & at higher speed, fraction of molecules of O_2 will be greater than that of SO_2 .

Ans. B

Sol. $M_{O_2} = \frac{1}{2} M_{SO_2}$

$$\therefore \text{if } T_{O_2} = \frac{1}{2} T_{SO_2}$$

$$\text{then } \frac{M_{O_2}}{T_{O_2}} = \frac{M_{SO_2}}{T_{SO_2}}$$

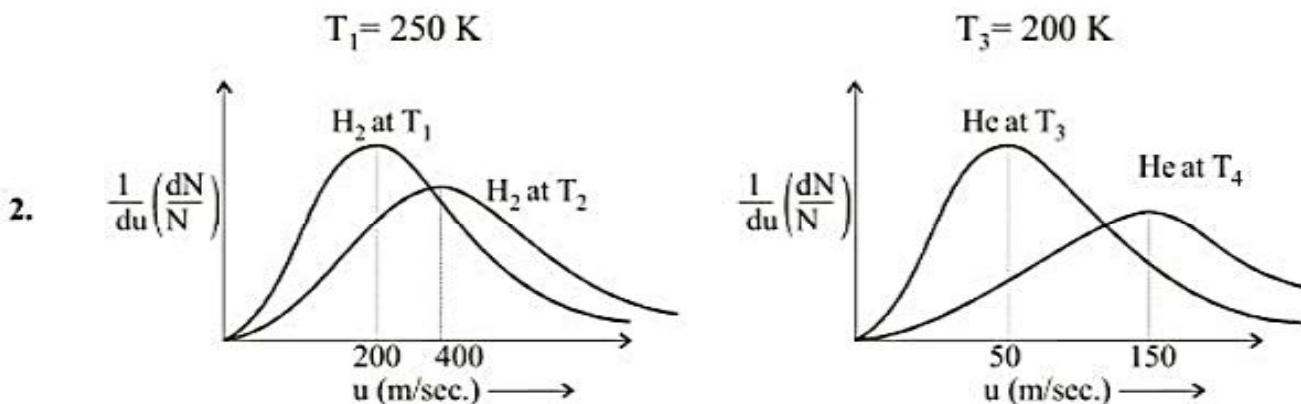
\therefore All other parameters are same \therefore the curves will be same
option (B)

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224327.jpg

Exercise**1. Find the true /false statement**

- (A) Most probable speed of ideal gases decreases with increase in molecular mass at constant temperature.
 (B) Number of particles moving with most probable speed decreases with increase in molecular mass for ideal gases.

Ans. (A) True (B) False



Select the correct option.

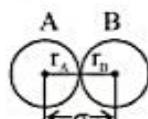
- (A) U_{mps} of H_2 at T_2 is greater than U_{mps} of He at T_4
 (B) U_{mps} of H_2 at T_2 is less than U_{mps} of He at T_4
 (C) U_{mps} of H_2 at T_2 is equal to U_{mps} of He at T_4
 (D) None of these

Ans. A

14. COLLISION THEORY**14.1 Collision diameter :**

It is the closest distance between the centres of two molecules taking part in collision.

$$\text{collision diameter } (\sigma) = r_A + r_B$$

**14.2 Collision Frequency :**

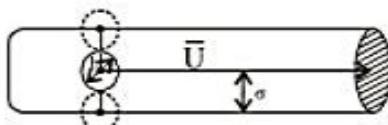
It is the number of molecular collisions taking place per second per unit volume of the gas.

Determination of number of bimolecular collisions :

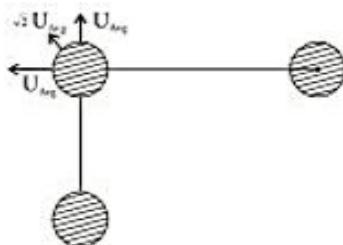
- (a) While considering the molecules among themselves the molecules to be rigid, non-interacting and spherical with diameter σ . It is also assumed that all the molecules move with the same speed. The arithmetic mean of speed is U_{Avg} .

Saved /storage/emulated/0/Pictures/TouchShot/
 20170808_224327.jpg

- (b) Two identical molecules of diameter σ will just touch each other when the distance separating their centres is σ . Thus, a moving molecule will collide with other molecules whose centres come within a distance of σ from its centre. The quantity $\pi\sigma^2$ is called the collision cross-section for the rigid spherical molecule. It is obvious that this collision cross-section is an area of an imaginary sphere of radius σ around the molecule within which the centre of another molecule cannot penetrate.



- (c) If the molecule is moving with an average speed U_{Avg} , then in a unit time area swept out by a single molecule is $\pi\sigma^2 U_{Avg}$. If N^* is the no. of molecules within the volume ($N^* = N/V$), the no. of collisions by a single molecule in a unit time will be $\pi\sigma^2 U_{Avg} N^*$.
- (d) So, far, we have assumed that only one molecule is moving and all other are stationary. In practice however, this is not true. In order to account for the movements of all molecules, we must consider the average velocity along the line of centre of two colliding molecules instead of average velocity of a single molecule. If it is assumed that, on average, molecules collide while approaching each other perpendicularly, then the average velocity along their centre is $\sqrt{2} U_{Avg}$ as shown below.



\therefore The no. of collisions made by a single molecule with other molecules per unit time (collision number) are given by

$$z_1 = \sqrt{2} \pi\sigma^2 U_{Avg} N^*$$

- (e) The total number of bimolecular collision per unit time is given z_{11} (collision frequency)

$$\begin{aligned} z_{11} &= \frac{1}{2} (z_1 N^*) = \frac{1}{2} \times N^* \times \sqrt{2} \pi\sigma^2 U_{Avg} N^* \\ &= \frac{1}{\sqrt{2}} \pi\sigma^2 U_{Avg} N^{*2} \end{aligned}$$

- (f) If the collisions involve two unlike molecules, the no. of biomolecular collision is given as z_{12} .

$$z_{12} = \frac{1}{\sqrt{2}} \pi\sigma_{12}^2 U_{12, Avg} N_1^* N_2^*$$

where N_1^* and N_2^* are the no. of molecules per unit volume of the two types of gases, σ_{12} is the average diameter of two molecules, that is,

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224328.jpg

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \text{ or } U_{12, \text{Avg}} = [U_{1, \text{Avg}}^2 + U_{2, \text{Avg}}^2]^{1/2}$$

$$U_{1, \text{Avg}}^2 = \frac{8RT}{\pi M_1}, \quad U_{2, \text{Avg}}^2 = \frac{8RT}{\pi M_2}$$

14.3 Determination of mean free path and its dependence on pressure and temperature :

- (a) The mean free path is the average distance travelled by a molecule between two successive collision. We can express it as follows :

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collisions made by single molecule per unit time}}$$

$$\lambda = \frac{U_{\text{Avg}}}{z_1} = \frac{U_{\text{Avg}}}{\sqrt{2}\pi\sigma^2 U_{\text{Avg}} N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

- (b) According to ideal gas equation,

$$PV = nRT = \frac{N}{N_A} RT$$

$$\text{or } P = \left(\frac{N}{V}\right) \left(\frac{R}{N_A}\right) T = \left(\frac{N^*}{V}\right) KT \text{ (where K is known as Boltzmann's constant)}$$

$$\text{Now } \frac{N}{V} = N^*$$

$$\therefore P = N^* KT \text{ or } N^* = \frac{P}{KT} \text{ or } N^* \propto \frac{P}{T}$$

$$(c) \quad \lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

$$\lambda = \frac{1}{N^*} \text{ or } \lambda \propto \frac{T}{P}$$

Since, according to gas law $P \propto T$ at constant volume

$\therefore \lambda = \text{constant at constant volume.}$

Thus there will no effect of changing T or P on λ . If the volume of the gas is kept constant.

$$(d) \quad \text{Now } z_1 = \sqrt{2} \pi \sigma^2 U_{\text{Avg}} N^*$$

$$U_{\text{Avg}} \propto \sqrt{T} \quad \therefore U_{\text{Avg}} = K_1 \sqrt{T}$$

$$N^* \propto \frac{P}{T} \quad \therefore N^* = K_2 \frac{P}{T}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224329.jpg

$$\therefore z_1 = \sqrt{2} \pi \sigma^2 K_1 K_2 \frac{P}{\sqrt{T}}$$

Now $z_1 \propto P$ when T constant

and $z_1 \propto \frac{1}{\sqrt{T}}$ when pressure is held constant.

At constant volume $P \propto T$ or $P = K'' T$

$$\therefore z_1 = \frac{K' K'' T}{\sqrt{T}}$$

or $z_1 \propto \sqrt{T}$ when volume is constant.

Again $z_1 \propto \sqrt{P}$ when volume is constant

$$(e) z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{Avg} N^{*2}$$

or $z_{11} \propto U_{Avg} N^{*2}$

$$\text{or } z_{11} \propto \sqrt{T} \left(\frac{P}{T} \right)^2$$

$$\text{or } z_{11} \propto \frac{P^2}{T^{3/2}}$$

Thus $z_{11} \propto p^2$ when temperature is held constant and $z_{11} \propto T^{-3/2}$ when pressure is held constant

At constant volume

$$z_{11} \propto T^{-1/2} \text{ and } z_{11} \propto P^{1/2}.$$

Illustration

Calculate the mean free path in CO_2 at 27°C and a pressure of 10^{-9} bar. (molecular diameter = 500 pm)

$$[\text{Given : } R = \frac{25}{3} \text{ J mol}^{-1} \text{ K}^{-1}, \sqrt{2} = 1.4, \pi = \frac{22}{7}, N_A = 6 \times 10^{23}]$$

$$\begin{aligned} \text{Sol. } \lambda &= \frac{KT}{\sqrt{2}\pi\sigma^2 P} = \frac{R}{N} \times \frac{T}{\sqrt{2}} \times \pi \sigma^2 P \\ &= \frac{25}{3} \times \frac{300}{6 \times 10^{23}} \times \frac{7}{1.4 \times 22 \times (500 \times 10^{-10})^2 \times 10^{-9} \times 10^5} \\ &= 0.0378 \times 10^3 \text{ ms}^{-1} \\ &= 3.78 \times 10^3 \text{ cms}^{-1} \end{aligned}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224329.jpg

Exercise

The mean free path of the molecule of a certain gas at 300 K is 2.0×10^{-5} m. The collision diameter of the molecule is 0.2 nm. Calculate

- number of molecules per unit volume of the gas, and
- pressure of the gas

$$[\text{Given : } R = \frac{25}{3} \text{ J mol}^{-1} \text{ K}^{-1}, \frac{1}{\sqrt{2 \times \pi}} = 0.225, N_A = 6 \times 10^{23}]$$

Ans. (a) $2.81 \times 10^{23} \text{ m}^{-3}$ (b) $1.17 \times 10^3 \text{ Pa}$

15. REAL GAS

Although the ideal gas model is very useful, it is only an approximation of the real nature of gases, and the equations derived from its assumptions ($PV = nRT$) are not entirely dependable. As a consequence, the measured properties of a real gas will often differ from the properties predicted by our calculations. The properties of real gas differ basically of two factors one is force of attraction between molecules and volume of gas molecules.

15.1 Difference between real gas & Ideal gas

S.No.	Ideal gas	Real gas
1.	Obeys gas law under all conditions of P and T.	Obeys only at low P and T.
2.	Obeys ideal gas equation	Does not obeys ideal gas equation
3.	Intermolecular interaction between gaseous molecules are negligible.	Intermolecular interaction between gaseous molecules not negligible.
4.	Volume of a particle is negligible as compared to total volume of the gas.	Volume of a particle is not negligible as compared to total volume of the gas
5.	Exists only at high temperature and low pressure	Exists only at low temperature and high pressure

Explanation of deviation

Kinetic theory of gases do not hold good at all condition mostly these two assumptions

- The force of attraction between gaseous molecules are negligible
- The volume occupied by the gaseous molecules is negligible compared to total volume of gas at high pressure. Both the assumptions do not hold good hence deviating from ideal gas.

16. VANDER WAALS EQUATION OF STATE FOR A REAL GAS

The equation of state generated by Vander Waals in 1873 reproduces the observed behaviour with moderate accuracy. For n moles of gas, the Vander Waals equation is

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

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224330.jpg

where a and b are constants characteristic of a gas. This equation can be derived by considering a real gas and converting it to an ideal gas.

- 16.1 Volume Correction :** We know that for an ideal gas $P \times V = nRT$. Now in a real gas the molecular volume cannot be ignored and therefore let us assume that 'b' is the volume excluded (out of the volume of container) for the moving gas molecules per mole of a gas. Therefore due to n moles of a gas the volume excluded would be nb .

∴ a real gas in a container of volume V has only available volume of $(V - nb)$ and this can be thought of, as an ideal gas in a container of volume $(V - nb)$

The Vander Waals constant b (the excluded volume) is actually 4 times the volume of a single molecule. i.e. $b = 4 N_A V$ where $N_A \longrightarrow$ Avogadro number.

$$\therefore b = 4 \times 6.023 \times 10^{23} \frac{4}{3} \pi r^3, \text{ where } r \text{ is the radius of a molecule.}$$

- 16.2 Pressure Correction :** Let us assume that the real gas exerts a pressure P . The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are not assumed to be exerting pressure.

It can be seen that pressure the real gas exerts would be less than the pressure an ideal gas would have exerted. Therefore if a real gas exerts a pressure P , then an ideal gas would exert a pressure equal to $P + p$ (p is the pressure lost by the gas molecules due to attractions). This small pressure p would be directly proportional to the extent of attraction between the molecules which are hitting the container wall and the molecules which are attracting these.

Therefore $p \propto \frac{n}{V}$ (concentration of molecules which are hitting the container's wall)

$$p \propto \frac{n}{V} \text{ (concentration of molecules which are attracting these molecules)} \Rightarrow p \propto \frac{n^2}{V^2}$$

$$\therefore p = \frac{an^2}{V^2}$$

where a is the constant of proportionality which depends on the nature of gas. Higher value of 'a' reflects the increased attraction between gas molecules.

- 16.3 The constant a and b :** Vander Waals constant for attraction (a) and volume (b) are characteristic for a given gas. Some salient features of 'a' and 'b' are:

- (i) For a given gas Vander Waal's constant of attraction 'a' is always greater than Vander Waals constant of volume (b).
- (ii) The gas having higher value of 'a' can be liquified easily and therefore H_2 and He are not liquified easily.
- (iii) The units of $a = \text{litre}^2 \text{ atm mole}^{-2}$ and that of $b = \text{litre mole}^{-1}$
- (iv) The numerical values of a and b are in the order of 10^{-1} to 10^{-2} to 10^{-4} respectively.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224330.jpg

Illustration

Identify true statement about the vander waal constant 'b' among the statements given below ?

- I. It is called excluded volume
- II. It accounts for the interparticle forces
- III. Its units are mol dm⁻³
- IV. Its value depends on molecular size

Ans. I, IV

Exercise

Among the four statements given below for real gases, which are correct :

- (A) The molecules causes attractive interactions.
- (B) They show deviation from ideal gas laws.
- (C) The molecules are volume less points.
- (D) The molecules have negligible mass.

Ans. A, B

Note : The Vander Waal equation can be obtained from ideal gas equation if 'P' is read as pressure exerted when all the intermolecular attractions are removed & 'V' is read as free volume available for the motion of molecules. The inclusions of correction terms, then will give the Vander Waal equation.

17. COMPRESSIBILITY FACTOR

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the compressibility factor, denoted by Z. It is defined as

$$Z = \frac{PV}{nRT}$$

The deviations from ideality may be shown by a plot of the compressibility factor Z, against P. For an ideal gas, Z = 1 and it is independent of temperature and pressure.

The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1.

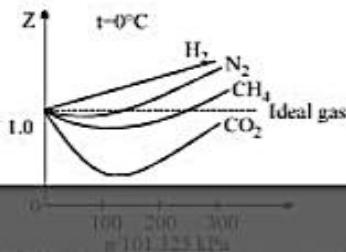
The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of non ideality of the gas.

For a real gas, the deviations from ideal behaviour depends on :

- (i) pressure ; and (ii) temperature.

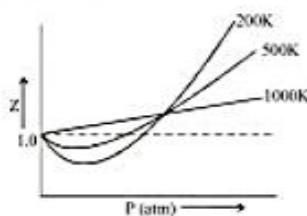
This will be illustrated by examining the compressibility curves of some gases discussed below with the variation of pressure and temperature.

17.1 Effect of Pressure Variation on Deviations:



Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224331.jpg

17.2 Effect of Temperature on Deviations:



From the above curves we can conclude that:

- At low pressure and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.
- At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.
- The closer the gas is to the liquefaction point, the larger will be the deviation from the ideal behaviour.

Greater is the departure of Z from unity, more is the deviation from ideal behaviour.

- (i) When $Z < 1$, this implies that gas is more compressible.
- (ii) When $Z > 1$, this means that gas is less compressible.
- (iii) When $Z = 1$, the gas is ideal.

17.3 Explanation of deviation by Van der Waals equation

- (i) **At lower pressure :** 'V' is large and 'b' is negligible in comparison with V.
Then Vander Waals equation reduces to :

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

$$PV = RT - \frac{a}{V} \Rightarrow Z = \frac{PV}{RT} = 1 - \frac{a}{VRT}, z < 1$$

or $PV < RT$ at low pressure (below Boyle temperature)
this accounts for the dip in PV vs P isotherm at low pressure.

- (ii) **At fairly high pressures :** $\frac{a}{V^2}$ may be neglected in comparison with P.

The Vander Waals equation becomes

$$P(V-b) = RT \Rightarrow PV - Pb = RT$$

$$PV = RT + Pb \Rightarrow Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}, z > 1$$

or $PV > RT$ at higher pressure (above Boyle temperature)

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

- (iii) **At very low pressure :** V becomes so large that both b and $\frac{a}{V^2}$ become negligible and the Vander Waals equation reduces to $PV = RT$

$$Z = \frac{PV}{RT} = 1 + Pb = \frac{a}{V^2} \quad \text{At extremely low pressure (at Boyle temperature)}$$

This shows why gases approach ideal behaviour at very low pressures.

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224331.jpg

- (iv) ***Hydrogen and Helium*** : These are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extensively small. So $\frac{a}{V^2}$ is negligible even at ordinary temperatures. Thus **PV > RT**.

Illustration

1. A real gas obeying vander waal equation will resemble ideal gas if the
(A) constants a and b are negligibly small (B) a is large and b is small
(C) a is small and b is large (D) constant a and b are large

Ans. A

Sol. At negligible small value of a, b , real gas reduces to ideal gas equation

2. The compressibility factor for 1 mole of a van der Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant, a .

Sol. For 1 mole of the gas,

$$Z = \frac{pV}{RT} \Rightarrow 0.5 = \frac{100 \times V}{0.0821 \times 273}; V = 0.112 \text{ L}$$

Neglecting b , van der Waals equation reduces to $\left(P + \frac{a}{V^2}\right)V = RT$

$$\text{or } pV + \frac{a}{V} = RT$$

$$\text{or } 100 \times 0.112 + \frac{a}{0.112} = .0821 \times 273$$

$$a = 1.25 \text{ L}^2\text{atm mol}^{-2}$$

Exercise

1. The compressibility factor of real gas is usually greater than one ($Z > 1$) at high temperature and high pressure. This is because
(A) the constant a is negligible while b is not (B) the constant b is negligible while a is not
(C) both a and b are negligible (D) both a and b are no negligible

Ans. A

2. The value of vander Waal's constant 'a' for the gases O₂, N₂, NH₃ and CH₄ are 1.36, 1.39, 4.17 and 2.253 J atm, m^{-2} , respectively. The gas which can most easily be liquefied is
 (A) O₂ (B) N₂ (C) NH₃ (D) CH₄

Ans. C

[Hint - Higher the value of a , easier is the liquification process)

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224332.jpg

18. OTHER EQUATIONS FOR REAL GAS

I. Dieterici Equation (for n mole of gas)

$$P(V - nb) = n R T e^{a/VRT}$$

2. Berthelot Equation (for n mole of gas)

$$\left(P + \frac{n^2 a}{T V^2} \right) (V - nb) = n R T$$

3. Virial Equation Of State (for n mole of gas)

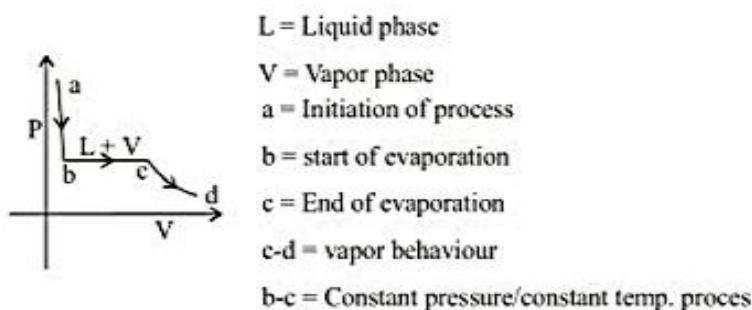
$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

$$B = \text{second virial coefficient, temperature dependent} = b - \frac{a}{RT}$$

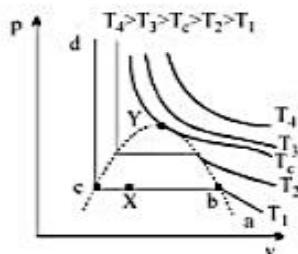
$$C = \text{third virial co-efficient, temperature dependent} = b^2$$

19. CRITICAL PHENOMENON & LIQUIFICATION OF GASES

Liquification process is executed by applying pressure at constant temperature and corresponding, a graph is plotted in P vs V (called andrew's Isotherm)



If similar isotherm are plotted at various temperature we get a graph as below.



The phenomena of converting a gas into liquid is known as liquifaction. The liquifaction of gas is achieved by controlling P and T as follows :

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224332.jpg

19.1 Methods of Liquification of Gases

- (a) On increasing the pressure gas can be easily liquified because intermolecular attraction between gaseous molecule increases.
 - (b) On decreasing the temperature K.E. of gaseous molecules decrease That's why gas can be easily liquified.
 - (c) Temperature of gas must be lower than critical temperature (T_C)

19.2 Critical temperature (T_c) : It is defined as the characteristic temperature for a given gas below which a continuous increase in pressure will bring liquification of gas and above which no liquefaction is noticed although pressure may be increased e.g. T_c for CO₂ is 31.2°C.

$$\text{For a Vanderwaal gas : } T_c = \frac{8a}{27Rh}$$

19.3 Critical pressure (P_c) : It is defined as the minimum pressure applied on 1 mole of gas placed at critical temperature, to just liquefy the gas

$$\text{For a Vanderwaal gas : } P_c = \frac{a}{27b^2}$$

19.4 Critical Volume (V_c) : The volume occupied by 1 mole of gas placed at critical conditions.

For a Vanderwaal gas : $V_c = 3b$ (i.e. $P = P_c$ and $T = T_c$)

19.5 Calculation of critical constants

$$\Rightarrow \frac{P}{V_m^2} V_m^2 - Pb + \frac{a}{V_m^v} - \frac{ab}{V_m^v} - RT = 0 \quad \text{multiply by } \frac{V_m^2}{P}$$

$$\Rightarrow V - b V_m^2 + \frac{a}{p} V_m^v - \frac{ab}{p} - \frac{RT}{p} V_m^2 = 0$$

$$\Rightarrow V_m^2 - \left(b + \frac{RT_c}{P_c} \right) V_m^2 + \frac{a}{P_c} - \frac{ab}{P_c} = 0 \quad \dots \dots \dots (1)$$

Again

$$(\mathbf{V}_m - \mathbf{V}_1) (\mathbf{V}_m - \mathbf{V}_2) (\mathbf{V}_m - \mathbf{V}_3) = 0$$

At critical conditions $V_1 = V_2 = V_3 = V_s$

At critical conditions, gases occupy a definite volume so all the 3 roots will be equal to v .

$$\therefore (V_m - V_o)^3 = 0$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224333.jpg

Comparing equation (i) & (ii)

$$3 V_c = b + \frac{RT_c}{p_c} \dots\dots\dots(3)$$

$$3 V_c^2 = \frac{a}{p_c} \dots\dots\dots(4)$$

$$V_c^3 = \frac{ab}{p_c} \dots\dots\dots(5)$$

Dividing (5) equation by (4) equation

$$V_c = 3b$$

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

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

Alternative method

- (i) From the graph value of slope at critical conditions is zero

$$\therefore \frac{dP}{dV} = 0$$

- (ii) Before & after the critical point the slope is negative therefore at critical point slope is max.

$$\therefore \frac{d^2P}{dV^2} = 0$$

For 1 mole

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

$$\Rightarrow P = \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \dots\dots\dots(1)$$

$$\therefore \frac{dp}{dv} = 0 \quad \therefore RT \frac{d[(v_m - b)^{-1}]}{dv} - \frac{ad[V_m^{-2}]}{dv} = 0$$

$$-\frac{RT}{(v_m - b)^2} + \frac{2a}{v_m^3} = 0 \dots\dots\dots(2)$$

and $\frac{d^2p}{dv^2} = \frac{2RT}{v_m^3} - \frac{6a}{v_m^5} = 0$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224334.jpg

On solving equation (1), (2), (3)

$$V_c = 3b$$

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

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

20. BOYLE'S TEMPERATURE

It is the temperature of which a gas behave ideally in a wide range of pressure.

20.1 Conversion of Vander Waal's equation in virial form Vander Waal's equation for 1 mole

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

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

$$\frac{PV_m}{RT} = \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \frac{V_m}{RT}$$

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

$$Z = \left(\frac{V_m - b}{V_m} \right)^{-1} - \frac{a}{V_m RT}$$

$$Z = \left[1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} \dots \right] - \frac{a}{V_m RT}$$

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

$$\therefore B = \left(b - \frac{a}{RT} \right); C = b^2; D = b^3$$

20.2 For the gas to behave ideally $B = 0$

as the subsequent terms are very small and does not influence much [at low pressure $P \rightarrow 0$]

$$\therefore B = 0$$

$$b - \frac{a}{RT} = 0$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224334.jpg

$$b = \frac{a}{RT}$$

$$T_B = \frac{a}{Rb}$$

Hence it is the temp at which the gas obeys Boyle's law.

Illustration

The compressibility factor for 1 mole of a Vander Waal's gas at Boyle temperature is

- (A) $1 + \frac{b^2}{V(V-b)}$ (B) $1 - \frac{b}{V}$ (C) $1 + \frac{b}{V}$ (D) $1 - \frac{b^2}{V^2}$

Ans. A

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$Z = \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{VRT}$$

$$= \frac{V}{V-b} - \frac{b}{V} \quad \left(T = \frac{a}{Rb} \right)$$

$$= 1 + \frac{b^2}{V(V-b)}$$

Exercise

Select correct statement for a real gas.

- (A) Larger the value of $\frac{T_c}{P_c}$ of gas, larger would be the excluded volume.
 (B) Critical temperature (T_c) of a gas is greater than Boyle's temperature (T_b).
 (C) At critical point in the Vander Waal's gas isotherm $\left(\frac{\partial P}{\partial V} \right)_{T_c} = 0$
 (D) For a real gas $T_c = 30^\circ C$ then it is gas at $25^\circ C$ & vapour at $35^\circ C$ always.

Ans. A, C

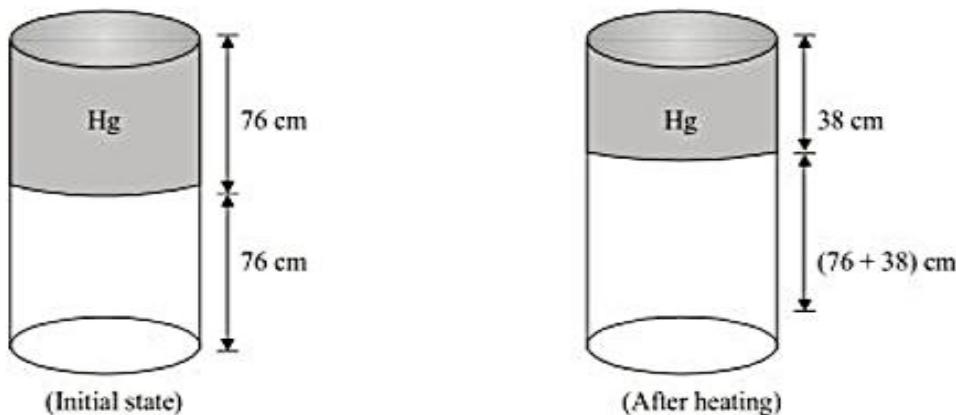
Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224335.jpg

SOLVED EXAMPLES

- Q.1** A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.

Ans. 337.5 K

Sol.



At initial stage :

$$\begin{aligned}\text{Pressure of gas} &= \text{Pressure of Hg} + \text{Pressure of atmospheric air} \\ &= 76 + 76 = 152 \text{ cm} \\ T &= 300 \text{ K}\end{aligned}$$

$$V = \frac{V_1}{2} \text{ where, } V_1 \text{ is volume of cylinder.}$$

At final stage after heating :

$$\begin{aligned}\text{Pressure of gas} &= \text{Pressure of Hg} + \text{pressure of atmospheric air} \\ &= 38 + 76 = 114 \text{ cm}\end{aligned}$$

$$V = \frac{3V_1}{4}, T = ?$$

Applying gas equation

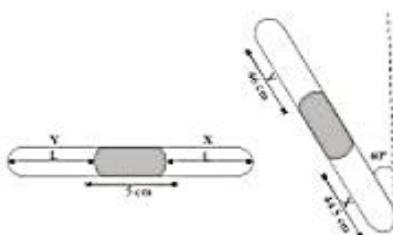
$$\begin{aligned}\frac{152 \times V_1}{2 \times 300} &= \frac{114 \times (3V_1 / 4)}{T} \\ T &= \frac{114 \times 3 \times 2 \times 300}{4 \times 152} = 337.5 \text{ K}\end{aligned}$$

- Q.2** A thin tube of uniform cross-section is sealed at both ends. It lies horizontally, the middle 5 cm containing Hg and the two equal ends containing air at the same pressure P_0 . When the tube is held at an angle 60° with the vertical, the lengths of the air column above and below the mercury are 46 and 44.5 cm respectively.

Calculate pressure P_0 in cm of Hg. (The temperature of the system is kept at 30°C .)

Ans. 75.4 cm of Hg

**Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224335.jpg**



Sol.

At horizontal position, let the length of air column in tube be L cm.

$$\therefore 2L + 5 = 46 + 5 + 44.5 \\ L = 45.25 \text{ cm}$$

when the tube is held at 60° with the vertical, the mercury column will slip down.

$$P_Y + 5 \cos 60^\circ = P_X$$

$$P_X - P_Y = \frac{5}{2} = 2.5 \text{ cm Hg} \quad \dots \dots \dots \text{(i)}$$

$$\text{From end X, } P_0 \times 45.25 = P_X \times 44.5$$

$$P_X = \frac{45.25}{44.5} P_0 \quad \dots \dots \dots \text{(ii)}$$

$$\text{From Y, } P_0 \times 45.25 = P_Y \times 46$$

$$P_Y = \frac{45.25}{46} P_0 \quad \dots \dots \dots \text{(iii)}$$

Substituting the values of P_X and P_Y in equation (i) we get

$$P_0 = 75.4$$

- Q.3** At fixed temperature and 600 mm pressure, the density of a gas is 42. At the same temperature and 700 mm pressure, what is the density of the gas?

Ans. 49

Sol. According to Boyle's law,

$$P \propto \frac{1}{V} \text{ (at constant temperature)}$$

$$\text{Density } D = \frac{\text{Mass (M)}}{\text{Volume (V)}}$$

$$\text{or } D \propto \frac{1}{V}$$

$$P \propto D$$

$$\frac{P_1}{D_1} = \frac{P_2}{D_2}$$

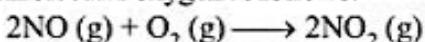
$$D_2 = \frac{P_2 \times D_1}{P_1}$$

$$P_1 = 600, D_1 = 42, P_2 = 700$$

$$D_2 = \frac{700 \times 42}{600} = 49$$

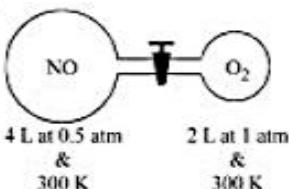
Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224337.jpg

Q.4 Nitric oxide (NO) reacts with molecular oxygen as follows:



Initially NO & O₂ are separated as shown below. When the valve is opened, the reaction quickly goes to completion. Determine what gases remains at the end of reaction and calculate their partial pressures. Assume that the temperature remains constant at 27°C.

[Given : R = 0.08 atm.L / mole.K]



Ans. $P_{\text{O}_2} = \frac{1}{6} \text{ atm}; P_{\text{NO}_2} = \frac{1}{3} \text{ atm}$

Sol. Initially $n_{\text{NO}} = \frac{0.5 \times 4}{0.080 \times 300}$; $n_{\text{O}_2} = \frac{2 \times 1}{0.080 \times 300}$
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$

Initial	$\frac{2}{24.0}$	$\frac{2}{24.0}$	0
---------	------------------	------------------	---

at the end of reaction $- \quad \frac{1}{24} \quad \frac{2}{24} \Rightarrow \frac{1}{12}$

NO₂ & O₂ gases remains at the end of reactions. **Ans.**

$$V_{\text{total}} = 6 \text{ L}$$

$$\text{P.Pr of O}_2 \Rightarrow \frac{1}{24} \times \frac{0.080 \times 300}{6} \Rightarrow \frac{1}{6} \text{ atm or } 0.166 \text{ atm}$$

$$\text{P.Pr. of NO}_2 \Rightarrow \frac{1}{12} \times \frac{0.080 \times 300}{6} \Rightarrow 0.333 \text{ atm or } \frac{1}{3} \text{ atm}$$

Q.5 Average velocity of CO₂ at the temperature T₁K and maximum possible velocity of CO₂ at the temperature T₂ K is 9×10^{-4} cm second⁻¹ then calculate the value of T₁ and T₂.

Ans. T₁ = 1682.5 K, T₂ = 2143.4 K

Sol. Average velocity = $\sqrt{\frac{8RT}{\pi M}}$

and maximum possible velocity = $\sqrt{\frac{2RT}{M}}$

Average velocity = Maximum possible velocity = $9 \times 10^4 \text{ cm sec}^{-1} = 9 \times 10^2 \text{ meter/second}$

$$\therefore 9 \times 10^2 = \sqrt{\frac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}}$$

$$9 \times 10^2 = \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}}$$

On solving $T_1 = 1682.5 \text{ K}$

$T_2 = 2143.4 \text{ K}$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224338.jpg

Q.6 Calculate the average kinetic energy of 8 g-molecules of methane at 27°C in Joule.

Ans. 6.21×10^{-21} J

Sol. Total kinetic energy = $n\left(\frac{3}{2}RT\right)$

$$\text{Mole number in 8 gram methane} = \frac{8}{16} = 0.5$$

(Molecular weight of methane = 16)

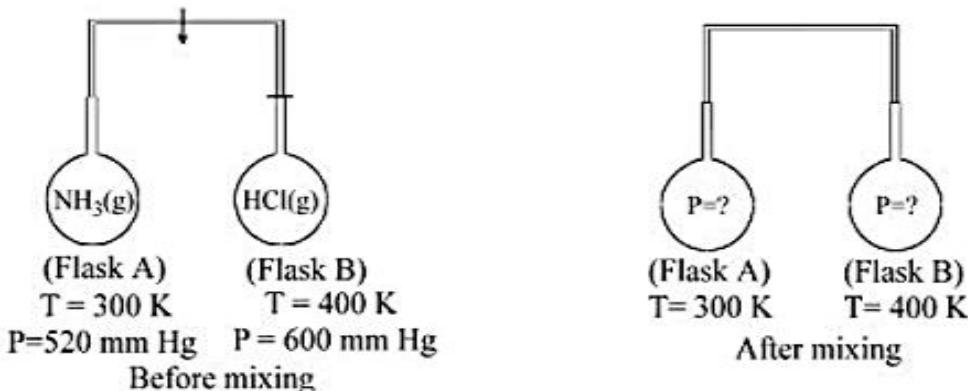
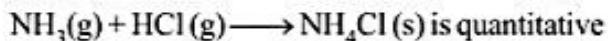
R = 8.314 Joule / K / mole

$$T = 27 + 273 = 300 \text{ K}$$

$$\text{Therefore, kinetic energy} = 0.5 \times \frac{3}{2} \times 8.314 \times 300 = 1870.65 \text{ Joule}$$

$$\therefore \text{Average kinetic energy} = \frac{1870.65}{6.023 \times 10^{23} \times 0.5} = 6.21 \times 10^{-21} \text{ joule}$$

Q.7 Two flasks A and B of equal volume containing NH_3 and HCl gases, are connected by a narrow tube of negligible volume. The two gases were prevented from mixing by stopper fitted in connecting tube. For further detail of experiment refer to the given figure. What will be final pressure in each flask when passage connecting two tubes are opened. Assume ideal gas behaviour of NH_3 and HCl gas and the reaction.



- (A) 40 mm Hg (B) 60 mm Hg (C) 20 mm Hg (D) 10 mm Hg

Ans. (A)

Sol. $P_{\text{HCl}} \text{ at } 300 \text{ K} = \frac{300}{400} \times 600 = 450 \text{ mm Hg}$

$$\text{Remaining } P = 520 - 450 = 70 \text{ mm Hg } \text{NH}_3 \text{ in flask 'A'}$$

Let 'x' is numbers of moles of NH_3 in 'A'

$$\Rightarrow \text{no. of mole of } \text{NH}_3 \text{ in B} = \frac{3}{4} x$$

$$\text{mole fraction of total mole remain in 'A'} = \frac{4}{7}$$

$$\text{Pressure in 'A'} = \frac{4}{7} \times 70 = 40 \text{ mm Hg} \text{ Ans.}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224339.jpg

Q.8 The graph of compressibility factor (Z) vs P for one mole of a real gas is shown in following diagram.

The graph is plotted at constant temperature 273 K. If the slope of graph at very high pressure $\left(\frac{dZ}{dp}\right)$

is $\frac{1}{10}$ atm $^{-1}$, the volume of one molecule of real gas in cm 3 is

[Given : $R = \frac{22.4}{273}$ L atm K $^{-1}$ mol $^{-1}$ and $N_A = 6 \times 10^{23}$]

- (A) 9.3×10^{-23} (B) 3.7×10^{-20} (C) 9.3×10^{-22} (D) 5.6×10^{-20}

Ans. (C)

Sol. At very high pressure

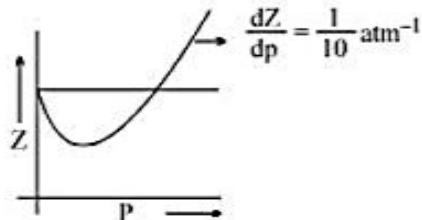
$$Z = 1 + \frac{Pb}{RT}$$

$$\frac{dZ}{dp} = \frac{b}{RT} = \frac{1}{10} \text{ atm}^{-1}$$

$$b = \frac{22.4}{273} \times \frac{273}{10} = 2.24 \text{ litre / mole}$$

$$b = 4 \times V \times N_A$$

$$V = \frac{2.24 \times 10^3}{4 \times 6 \times 10^{23}} \Rightarrow 9.3 \times 10^{-22} \text{ cc} \quad \text{Ans.}$$



Q.9 The diameters of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake-water and the atmosphere are equal what is the depth of the lake ? (The density of lake-water and Hg are 1 gm/ml and 13.6 respectively. Also neglect the contribution of pressure due to surface tension)

Ans. 65116.8 cm

Sol. The pressure on the bubble = 1 atm (when it is at the surface)

The pressure on the bubble = P atm (say) (when it is at the bottom)

$$\text{The volume of the bubble} = \frac{1}{6} \pi (0.1)^3$$

$$P \times \frac{1}{6} \pi \times (1.0)^3 = 1 \times \frac{1}{6} \pi (0.4)^3$$

or $P = 64$ atm. Thus the pressure due to water is 63 atm (atmospheric pressure = 1 atm)

Now, consider the depth of lake is h cm

$$\therefore 63 \times 76 \times 13.6 \times g = h \times 1 \times g$$

$$\text{or } h = 63 \times 76 \times 13.6 \text{ cm} = 65116.8 \text{ cm.}$$

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224340.jpg

- Q.10** A 10 cm volume of air is trapped by a column of Hg, 8 cm long in capillary tube horizontally fixed as shown below at 1 atm pressure. Calculate the length of air column when the tube is fixed at same temperature.

- (a) Vertically with open end up
- (b) Vertically with open end down
- (c) At 45° from with open end up

Ans. (a) 9.04 cm (b) 11.18 cm (c) 9.3 cm

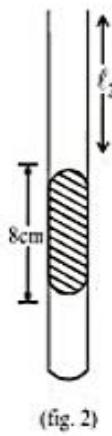
Sol. (a) When the capillary tube is held as vertically open end up (fig. 2),
The pressure on the air column = atmospheric pressure + pressure
of 8 cm Hg column

$$= 76 + 8 = 84 \text{ cm of Hg.}$$

Let, at this condition the length of the air column = ℓ_2
and the length of air column when capillary is horizontally
fixed = $\ell_1 = 10 \text{ cm}$ and pressure on air column = 1 atm.
Let the cross section of the capillary = $a \text{ cm}^2$

$$\therefore 76 \times 10 \times a = 84 \times \ell_2 \times a$$

$$\text{or } \ell_2 = \frac{76 \times 10}{84} = 9.04 \text{ cm}$$



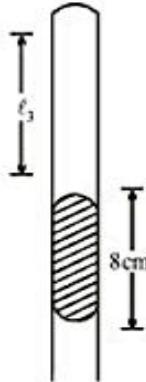
(fig. 2)

- (b) When the capillary tube is held as vertically open end down (fig. 3), the pressure on the air column

$$\begin{aligned} &= \text{atmospheric pressure} - \text{pressure of 8 cm Hg column} \\ &= 76 - 6 = 68 \text{ cm of Hg} \end{aligned}$$

Let at this condition the length of air column = ℓ_3 ,
 $\therefore 68 \times \ell_3 \times a = 76 \times 10 \times a$

$$\text{or } \ell_3 = \frac{76 \times 10}{68} = 11.18 \text{ cm}$$



(fig. 3)

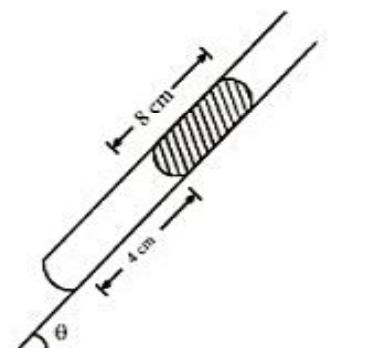
- (c) When the capillary is held at 45° with open end up, the weight of Hg is partially borne by the gas and partially by the Hg. The pressure on the gas due to Hg column
 $= 8 \times \cos 45^\circ$

$$= 8 \times \frac{1}{\sqrt{2}} = \frac{8}{\sqrt{2}} \text{ cm of Hg}$$

$$\therefore \text{total pressure on the gas} = \left(76 + \frac{8}{\sqrt{2}} \right) \text{ cm of Hg.}$$

Let length of air column at this pressure = ℓ_4 .

$$\therefore \ell_4 \times a \times \left(76 + \frac{8}{\sqrt{2}} \right) = 10 \times a \times 76$$



(fig. 4)

Saved /storage/emulated/0/Pictures/TouchShot/
20170808_224340.jpg

$$\therefore \ell_4 = \left(\frac{10 \times 76}{76 + 8/\sqrt{2}} \right) = 9.3 \text{ cm}$$

- Q.11** A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atmosphere at 27°C. If the cylinder can hold 2.82 litre of water at NTP, calculate the number of balloons that can be filled up.

Ans. 10

Sol. Radius of the balloon = $\frac{21}{2} \text{ cm} = 10.5 \text{ cm}$

$$\text{Volume of the balloon} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10.5)^3 \text{ cc} = 4851 \text{ cc}$$

$$\text{Pressure} = 1 \times 76 \times 13.6 \times 981 = 1.014 \times 10^6 \text{ dynes/cm}^2$$

$$\therefore \text{No. of mole of H}_2 \text{, the balloon can contain at NTP} = \frac{PV}{RT} = \frac{1.014 \times 10^6 \times 4851}{8.314 \times 10^7 \times 273} = 0.2167$$

$$\text{No. of mole in the cylinder} = \frac{20 \times 76 \times 13.6 \times 981 \times 2820}{8.314 \times 10^7 \times 300} = 2.2929$$

When the balloons are being filled, the pressure in the cylinder will decrease, when the pressure of the cylinder will drop to 1 atm, gas cannot be withdrawn.

$$\text{Now, no. of moles of H}_2 \text{ remaining in the cylinder unused} = \frac{1.014 \times 10^6 \times 2820}{8.314 \times 10^7 \times 300} = 0.1146$$

$$\therefore \text{No. of balloons that can be filled} = \frac{\text{No. of moles of H}_2 \text{ in the cylinder that can be used}}{\text{No. of moles of H}_2 \text{ in one balloon can contain}}$$

$$= \frac{2.2929 - 0.1146}{0.2167} = 10$$