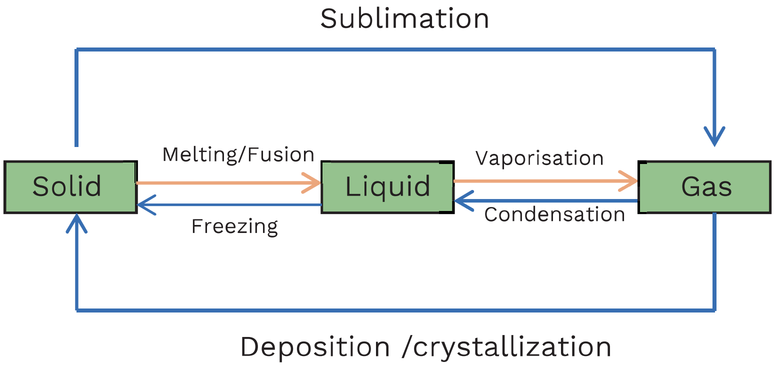
GASEOUS STATE

DISCLAIMER

Introduction

- Any matter can be physically classified as solid, liquid or gas which are most common physical states of matter on earth.



CHARACTERISTICS OF STATES OF MATTER

S.No.	Property	Solid	Liquid	Gas
1.	Intermolecular distance	Negligible	Moderate	Very large
2.	Intermolecular attraction	Very high	Moderate	Very low
3.	K.E. of particles	Zero	Low	Very high
4.	Shape	Definite	Indefinite	Indefinite
5.	Volume	Definite	Definite	Indefinite
6.	Density	High	Moderate	Very low
7.	Diffusion	Negligible	Yes/No	Always yes
8.	Compressibility	Negligible	Negligible	Compressibl

S.No.	Property	Solid	Liquid	Gas
9.	Type of mixture	Both	Both	Always homogenous

GASEOUS STATE

To describe a gas, minimum four parameters are required which are as following:

1. **Amount of gas:** Moles = $\dfrac{\text{mass}(\text{gm})}{\text{molar mass}(\text{g / mol})} = \dfrac{\text{No. of particles}}{N_A}$
2. **Temperature of gas:** T(in Kelvin) = T (°C) + 273
3. **Occupied volume of gas:** Every gas occupies the entire volume of the container in which it is kept (ideal gas case).

   Hence, V_{gas} = Volume of container
4. **Pressure of gas :**

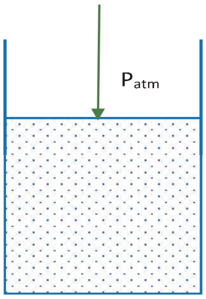
   In a gas sample present in a vessel, all particles move with high speeds and hence collide continuously with each other as well as with walls of container.
   - Hence it is considered that gas particles apply a uniform force on each point of the wall.
   - Since Pressure $= \dfrac{\text{Force}}{\text{Area}}$ so at each point on the wall of container, the pressure is same which is known as **pressure of gas**.

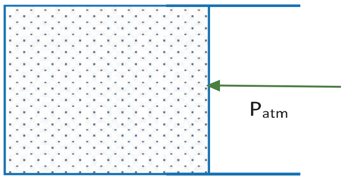
ATMOSPHERIC PRESSURE (P_{ATM})

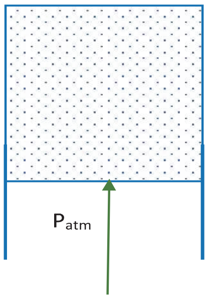
- The force applied by atmospheric gases per unit area of earth's surface is **known as atmospheric pressure.**

  Standard $P_{atm} = 1.01325 \times 10^5\ N/m^2 = 1$ atm
- Standard P_{atm} is defined at sea-level and as height from sea level increases, P_{atm} decreases.

  Note: In an apparatus, from every open end, P_{atm} is applied.







Calculation of pressure

- At any point, the pressure is due to all substances present above that point.
- Since all present at same horizontal level, pressure is same.

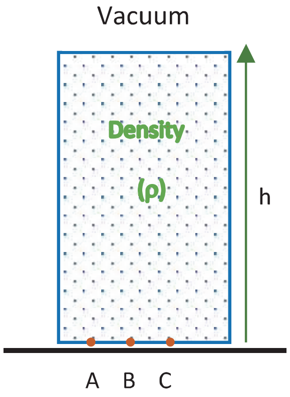
i.e. $P_A = P_B = P_C = P$ $[P_{vaccum} = 0]$

$$P = \frac{\text{Force}}{\text{Area}} + 0$$

$$\because P = \frac{mg}{A} = \frac{(V \times \rho)}{A} g = \frac{(A \times h)\rho g}{A}$$

$$\boxed{P = \rho g h}$$

$$\begin{pmatrix} \text{Force} = mg \\ m = \text{Volume} \times \text{density}(\rho) \\ \text{Volume} = \text{area} \times \text{height} \end{pmatrix}$$



Note: In above relation, all values must be put in S.I units only

i.e. ρ(density) = kg/m^3

g(gravitational constant) = 9.8 m/s^2

h(height) = meter

P(Pressure) = N/m^2 or Pascal

ILLUSTRATION:

Q1 **Calculate the pressure at point A in mercury column of given figure.**

A1 $P_A = P_{column} + P_{vacuum}$

$P_A = \rho g h + 0$

$= (13.6 \times 10^3 \text{ kg/m}^3)(9.8 \text{ m/s}^2)(76/100 \text{ m})$

$= 1.01325 \times 10^5 \text{ N/m}^2 = 1 \text{ atm}$

$= 76$ cm of Hg $= 760$ mm of Hg

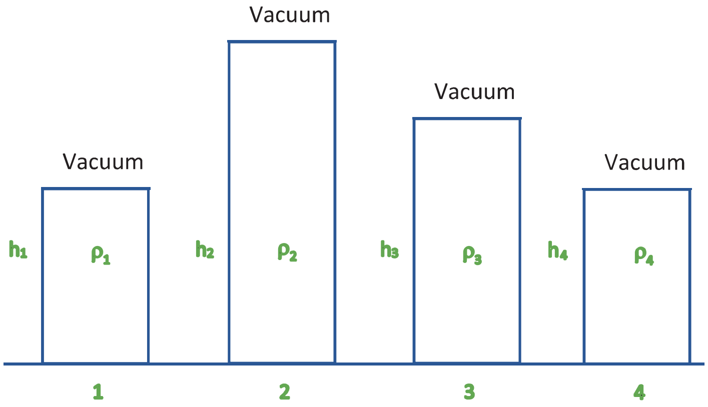
Q2 **Calculate height of water column which exerts 1 atm pressure at the bottom.**

A2 $P = \rho g h + 0$

$= (1.01325 \times 10^5 \text{ N/m}^2) = (1 \times 10^3 \text{ kg/m}^3)(9.8 \text{ m/s}^2)\, h$

$\Rightarrow h = 10.33 \text{ m} = 1033 \text{ cm}$

Note: If same pressure is applied at the bottom of different columns:



If $P_1 = P_2 = P_3 = P_4$

$\Rightarrow$ **$(\rho_1 h_1) = (\rho_2 h_2) = (\rho_3 h_3) = (\rho_4 h_4)$**

i.e For previous question

$$(1\ \text{atm})_{Hg} = (1\ \text{atm})_{H_2O}$$

13.6×76 cm $= 1 \times h$

$h = 1033$ cm

Q3 Calculate the pressure at A and B in the given figure (1) and figure(2).

A3

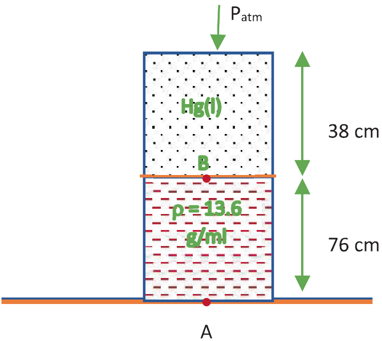


Figure (1)

(i) $P_A = (\rho.g.h) + P_{atm} = (114 \text{ cm of Hg}) + (1 \text{ atm})$
$= (1.5 \text{ atm}) + 1 \text{ atm} = 2.5 \text{ atm}$
$P_B = (\rho gh) + P_{atm}$
$= (0.5 \text{ atm}) + 1 \text{ atm}$
$= 1.5 \text{ atm}$

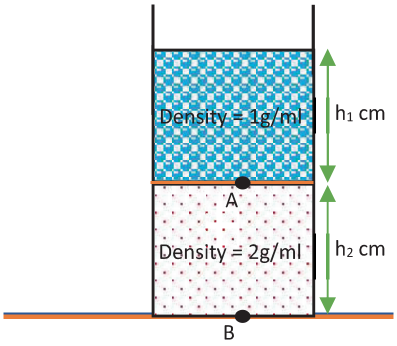


Figure (2)

(ii) $P_A = (\rho_1.g.h_1) + P_{atm}$

and $P_B = (\rho_2 g h_2) + (\rho_1 g h_1) + P_{atm}$
or $P_B = (\rho_2 g h_2) + P_A$

BAROMETER

A device used to measure atmospheric pressure.

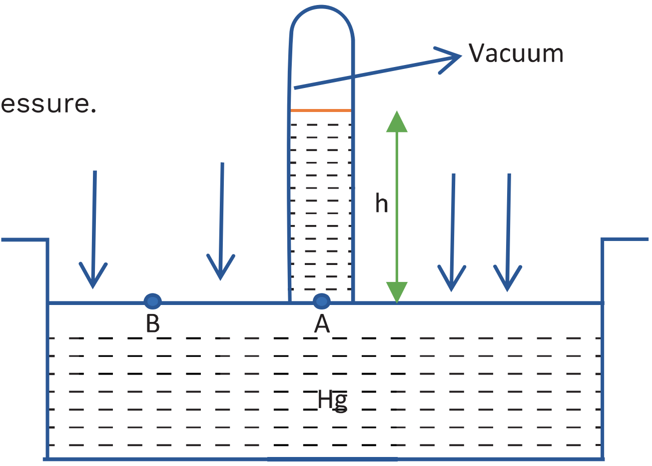
$P_A = \rho.g.h + 0$

$P_B = P_{atm}$

$\because$ A and B same level i.e. $P_A = P_B$

$P_{atm} = \rho.g.h$

i.e. at sea level, h = 76 cm



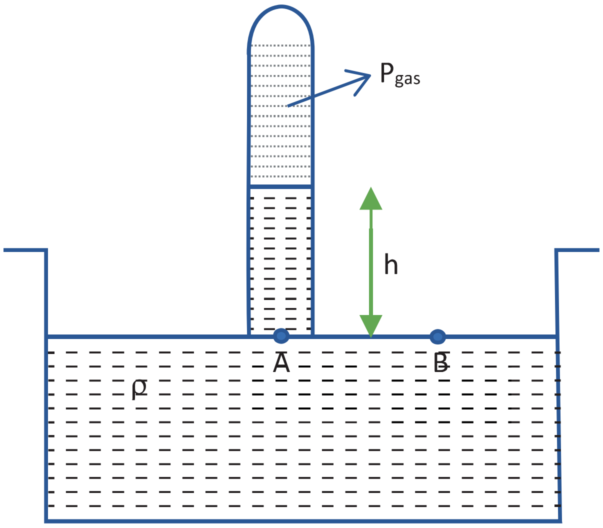
$P_A = (\rho.g.h) + P_{gas}$

$P_B = P_{atm}$

$\because$ $P_A = P_B$

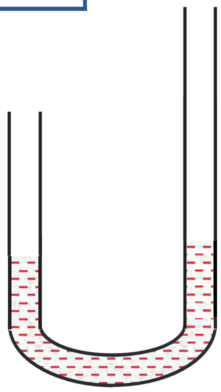
$\rho gh + P_{gas} = P_{atm}$

$$\boxed{P_{gas} = P_{atm} - \rho gh}$$



MANOMETER

- It is used to measure pressure of gas sample present in a vessel.
- It is a 'J' shaped glass tube filled with Hg(l).
- Smaller tube is called inner tube which will be connected to gas sample.
- Larger tube is called outer tube which may be open or closed.
- Before connecting to the gas, Hg level in both tubes is same, but after connecting the liquid moves and then a stable height difference of Hg levels in both columns is observed. Using that, pressure of gas is calculated.



- **Depending upon the outer tube, there are two types of monometer as following:**

1. CLOSED END MANOMETER

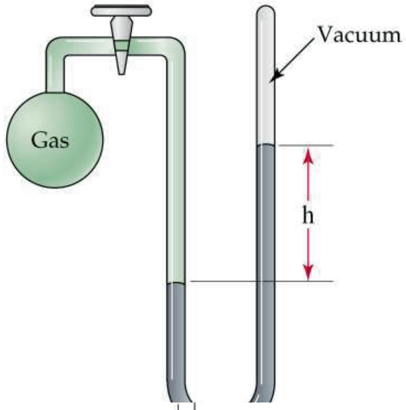
- Outer tube is closed.
- After connecting to the gas sample, liquid always moves inner to outer tube side.

$P_1 = P_{gas}$ and $P_2 = (\rho.g.h) + 0$

Since 1 and 2 are at same level

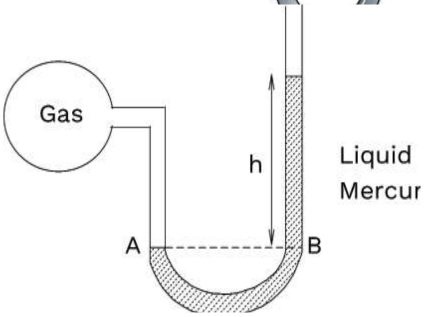
$P_1 = P_2$

$\Rightarrow \boxed{P_{gas} = \rho.g.h}$



2. OPEN END MANOMETER

- Open tube remains opened hence P_{atm} is applied.
- After connecting to the gas, there can be any of the following three possibilities.



CASE 1

$P_A = P_{gas}$ and $P_B = (\rho.g.h) + P_{atm}$

$P_A = P_B$

i.e. $P_{gas} > P_{atm}$

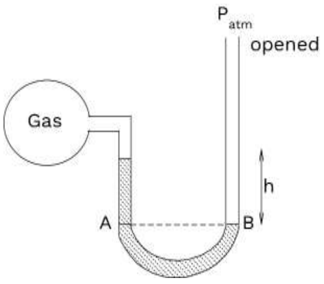
CASE 2

$P_A = (\rho gh) + P_{gas}$

$P_B = P_{Atm} \Rightarrow P_A = P_B$

$\Rightarrow P_{gas} = P_{atm} - (\rho gh)$

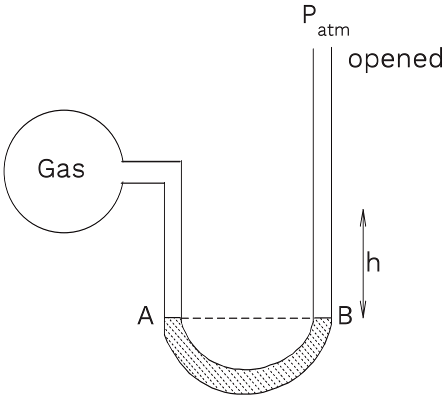
i.e. $P_{gas} < P_{atm}$



CASE 3

$P_A = P_{Gas}$

$P_B = P_{atm}$

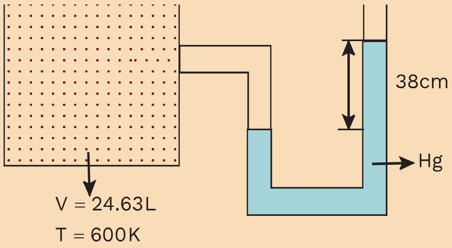


$P_A = P_B$

$\therefore\ P_A = P_{atm} \quad \Rightarrow P_{gas} = P_{atm}$

ILLUSTRATION:

Q1 **From the following set-up, calculate moles of the gas present in the container of volume 24.63 L at 600 K if the level of mercury in the open tube of the manometer is 38 cm higher.**
(Given: Atmospheric pressure = 76 cm of mercury)



A1 $P_{gas} = P_{atm} + P_{gh}$

= (76 cm of Hg) + (38 cm of Hg)

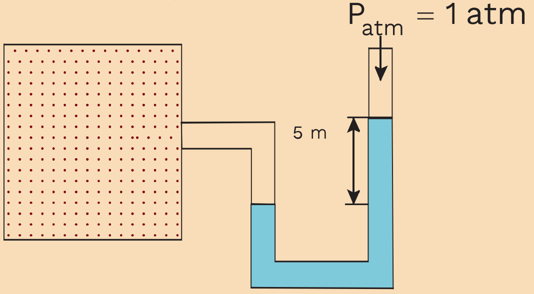
= 114 cm of Hg

PV = nRT

$$\left(\frac{114}{76}\right) \times 24.63 = n \times (2 \times 24.63) \Rightarrow n = 3/4 \text{ moles}$$

Q2 **Calculate the number of moles of gas present in the container of volume = 10 litre at 300 K. If the manometer containing glycerine shows 5 m difference in level as shown in diagram.**

(Given: $d_{glycerin}$ = 2.72 gm/ml, $d_{mercury}$ = 13.6 gm/ml)



A2 Height difference by glycerine = 5 m = 500 cm

Let height of mercury = h cm

5 m of glycerine ⇒ Hg

$(\rho.h)_{glycerine} = (\rho.h)_{Hg}$

$2.72 \times 500 \text{ cm} = 13.6 \times h$

h = 100 cm of Hg

Now, $P_{gas} = P_{atm} + \rho gh = 76 \text{ cm} + 100 \text{ cm} = 176$ cm of Hg

PV = nRT

$$\Rightarrow \frac{176}{76} \times 10 = n \times 24.6$$

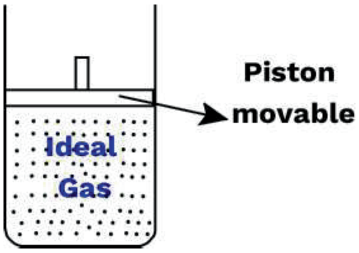
$$\Rightarrow n = \frac{176}{76} \times \frac{10}{24.6} = 0.94 \text{ moles}$$

Ideal Gas Law

IDEAL GAS

- The gas which obeys each and every point of kinetic theory of gases.
  Or
- The gas which obeys all gas laws is known as **Ideal gas**.
- Various gas laws are as following:

1. BOYLE'S LAW

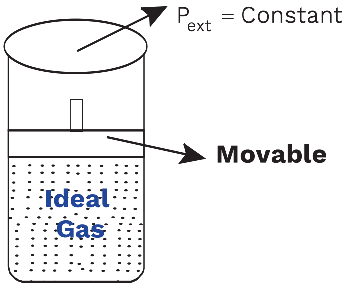


It states that volume of a fixed mass of gas is inversely proportional to its pressure at constant temperature.

$V \propto \frac{1}{P}$ (At constant n and T)

PV = constant

2. CHARLES LAW



It states that volume of given mass of gas at constant pressure is directly proportional to its temperature on the Kelvin scale.

$V \propto T$ (Kelvin) (At constant n and P)

i.e. $\frac{V}{T}$ = Constant

3. GAY LUSSAC'S LAW

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

$P \propto T$ (Kelvin) (At constant n and V)

$\Rightarrow \frac{P}{T}$ = constant

4. AVOGADRO'S LAW

It states that equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.

$n \propto V$ (At constant P and T)

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

Note: When all gas laws are combined together then Ideal gas equation is formed which is as following:

$\boxed{PV = nRT}$

Where R = Universal gas constant

= 0.0821 atm. lit. / mol. K

= 8.314 J /mol. K

= 2 cal / mol. K

GRAPHS

(A vs B)

By default, A $\longrightarrow$ y – axis

B $\longrightarrow$ x – axis

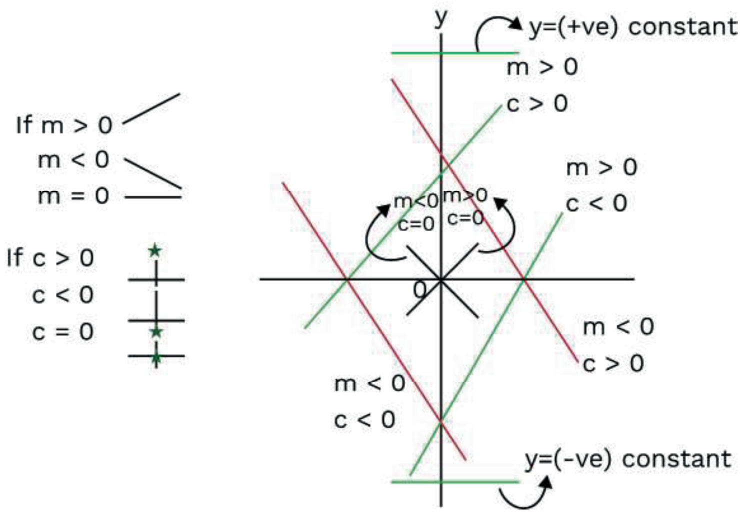
Equation between A and B in given condition.

Put A= y and B = x

$\Rightarrow$ Equation in terms of x and y

STRAIGHT LINE

General equation: y = mx + c

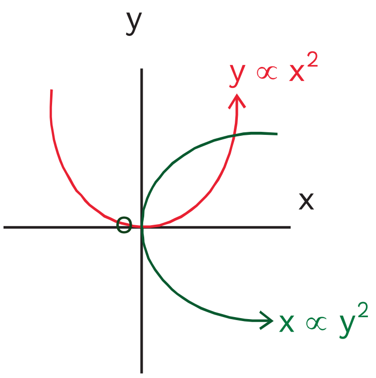


PARABOLA:

General equation

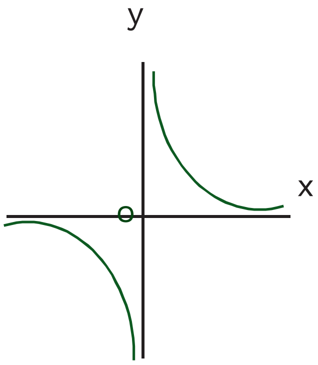
$y \propto x^2$

$x \propto y^2$



RECTANGULAR HYPERBOLA:

$xy = \text{constant}$

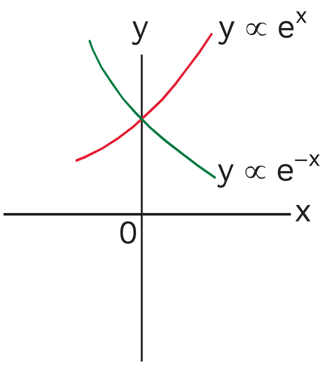


EXPONENTIAL:

$y \propto e^x$

and

$y \propto e^{-x}$



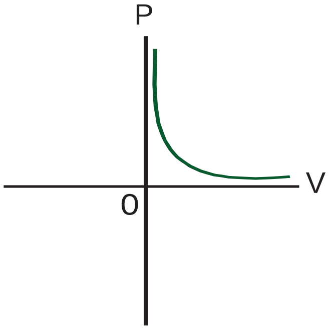
GRAPHS FOR BOYLE'S LAW (PV = CONSTANT)

i) P vs V

$P\ V = \text{constant}$

$xy = \text{constant}$

i.e. Rectangular hyperbola

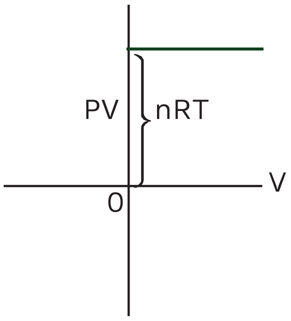


II) PV Vs V

PV vs V

$PV = \text{constant}$

$y = \text{constant}$

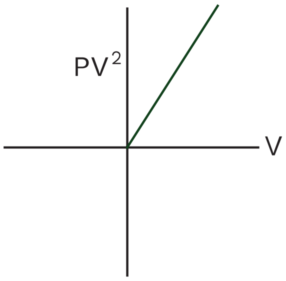


III) PV^2 Vs V

$PV = K \rightarrow \text{constant}$

$PV^2 = KV$

$y = kx$

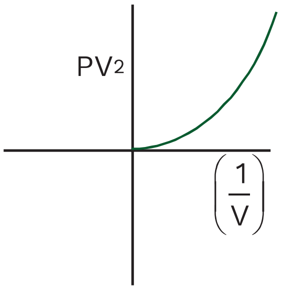


IV) $\left(\frac{P}{V}\right)$ vs $\left(\frac{1}{V}\right)$

$\therefore PV = K$

$$\frac{P}{V} = k\left(\frac{1}{V}\right)^2$$

$y = Kx^2$

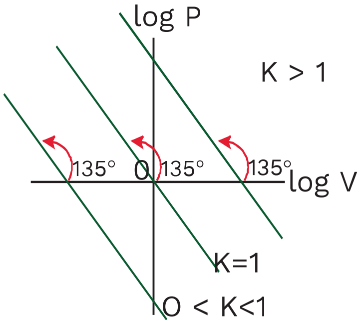


- **log (P) vs log (V) for Boyle's law**

$PV = K$

$\log(PV) = \log K$

$\log P + \log V = \log K$



$\Rightarrow y = -x + \log K$

On comparing with line equation, we get

$y = mx + c$

slope $= (-1)$

$\Rightarrow \theta = 135°$

and Intercept $= \log k$

V vs T(Kelvin) for Charles's Law :

$$\frac{V}{T(\text{Kelvin})} = K \qquad \left(K = \frac{nR}{P}\right)$$

$V = KT$

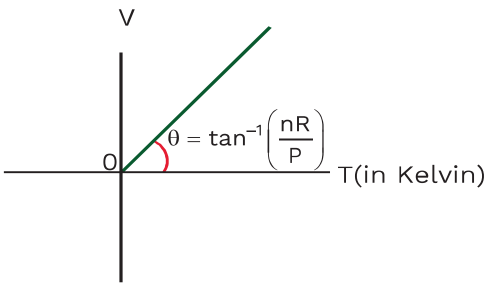
$\Rightarrow \quad y = k.x$

$y = mx$

On comparing with equation of straight line

$c = 0$

$$m = \frac{nR}{P} = \tan\theta$$



V vs T(°C) for Charles's Law:

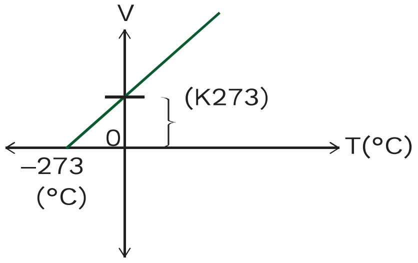
$V = KT(\text{in Kelvin})$

$V = K[T(°C) + 273]$

$V = K.T(°C) + K(276)$

$\Rightarrow \quad y = (k)\ x + (k.273)$

$m > 0 \qquad C > 0$

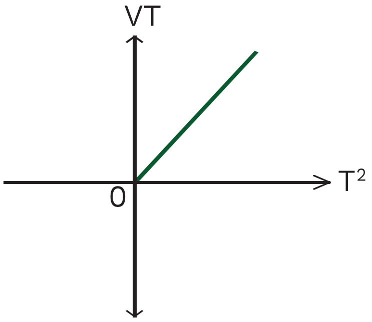


VT Vs T² FOR CHARLES'S LAW

$V = K.T$

$VT = KT^2$

$\Rightarrow \quad y = k.x$



log V vs log T for Charles's Law

$V = KT$

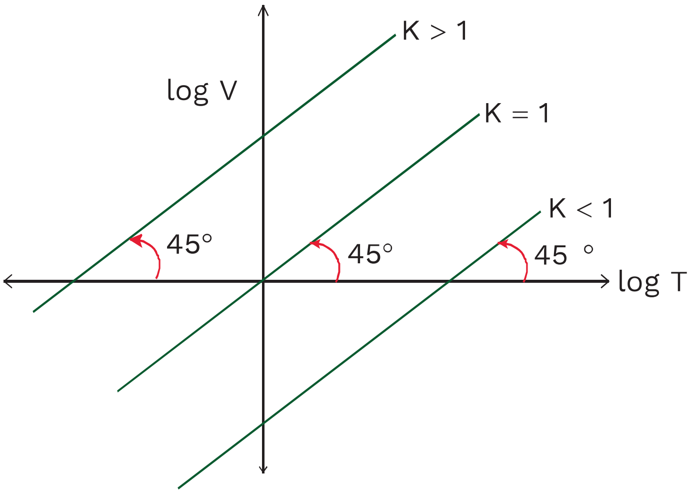
$\therefore \quad \log V = \log K + \log T$

$y = x + \log K$

$y = mx + c$

$m = (1) \Rightarrow \theta = 45°$

$c = \log\left(\frac{nR}{P}\right)$

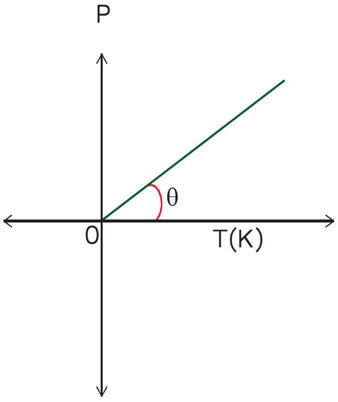


P vs T(K) FOR GAY LUSSAC'S LAW

$P = KT \qquad \left(K = \frac{nR}{V}\right)$

$\Rightarrow y = K.X$

$\tan\theta = K = \left(\frac{nR}{V}\right)$

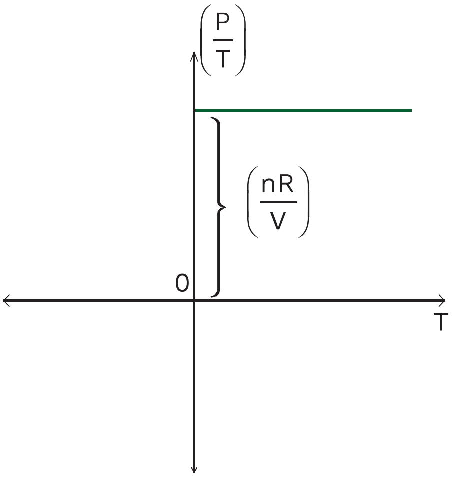


(P/T) vs T for Gay Lussac's law

$P = KT$

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

$\Rightarrow y = \text{constant}$

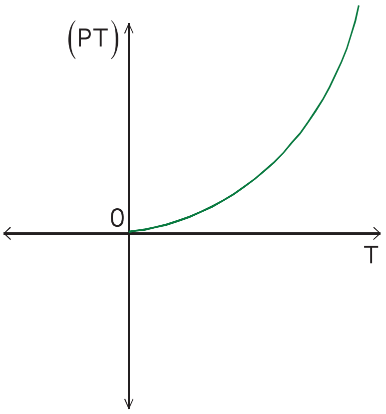


PT Vs T FOR GAY LUSSAC'S LAW

$P = KT$

$PT = KT^2$

$y = kx^2$

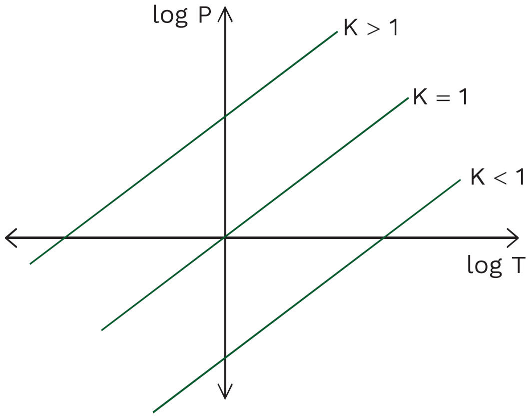


log P vs log T for Gay Lussac's Law

$$P = KT$$

$$\therefore \quad \log P = \log K + \log T$$

$$y = x + \log K$$



EQUATION OF STATE

An ideal gas present in a state, if subjected to another state:

$$\boxed{\begin{matrix} P_1 & \\ V_1 & \text{Ideal gas} \\ n_1, T_1 & \end{matrix}} \longrightarrow \boxed{\begin{matrix} P_2 & \\ V_2 & \text{Ideal gas} \\ n_2, T_2 & \end{matrix}}$$

State – 1

$\therefore P_1V_1 = n_1RT_1$

State – 2

$\therefore P_2V_2 = n_2RT_2$

$$\Longrightarrow \boxed{\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}}$$

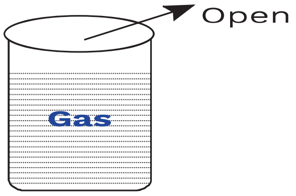
Equation of state

Dalton's Law

TYPES OF CONTAINER

1. Open Container

Atleast one wall must be open e.g. Drinking glass, Jug, Test Tube, Bucket etc.



$P_{gas} = P_{atm}$ (by default constant)

Also

$V_{container}$ = Constant

$\therefore$ PV = nRT

$$(n)_{gas} = \frac{K}{T}$$

If $T\uparrow \Rightarrow (n)_{gas} \Rightarrow$ gas escapes out and vice – versa.

If temperature increases then number of moles inside decreases.

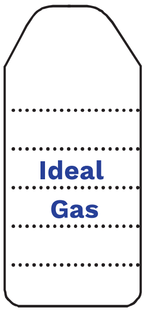
$\therefore$ Gas escapes out.

2. CLOSED RIGID CONTAINER

It is surrounded by rigid walls.

e.g. gas cylinder, closed room etc.

i.e.,



Volume = Constant

Moles = Constant (by default)

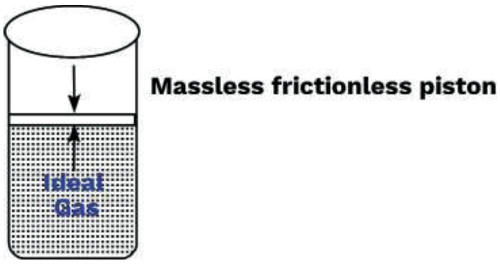
Note: If the gas takes part in a reaction then moles may be changed.

3. Closed non–rigid container

Atleast one wall must be movable e.g. piston–fitted vessel, balloon, bubble etc.

- If massless piston, $P_{gas} = P_{atm}$ (by default constant)
- If piston has mass, $P_{gas} = P_{atm} + P_{piston}$

i.e. $\boxed{P_{Gas} = \text{constant}}$ by default



Pv = nRT

$P \propto T$

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

- Case of open container

$P \propto nT$

$$\frac{P_1}{n_1T_1} = \frac{P_2}{n_2T_2}$$

- Case of rigid closed container

ILLUSTRATION:

Q1 **An amount of $CO_2(g)$ occupies 30 L at 27°C and 1 atm pressure. What would be the volume of same amount of $CO_2(g)$ collected at 227°C and 0.8 atm.**

A1 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\frac{1 \times 30}{300} = \frac{0.8 \times V_2}{500}$

$\Rightarrow V_2 = 62.5$ L

Q2 **A gas is present at a pressure of P_{atm}. Calculate the % increases in pressure, which should be done so that the volume of the gas can be decreased to $P_2 \times \frac{V}{4}$ of the initial volume if the temperature is maintained constant.**

A2 $P_1V_1 = P_1V_2$

$P \times V = P_2 \times \frac{V}{4}$

$\Rightarrow P_2 = 4P$

$\Rightarrow$ % increase in pressure = $\frac{\text{increase in P}}{\text{Inital P}} \times 100 = \frac{3P}{P} \times 100 = 300\%$

Q3 **Pressure of ideal gas contained in a closed rigid vessel is increased by 20% when it is heated by 60 K. Calculate its final temperature.**

A3 Closed rigid vessel $\Rightarrow$ V = constant, n=constant (by default)

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

$$\Rightarrow \frac{P}{(T-60)} = \frac{1.2P}{T}$$

$\Rightarrow$ T = 1.2(T–60)

T = 1.2T – 72

$\Rightarrow$ 72 = 1.2T – T

72 = 0.2T

$$\Rightarrow T = \frac{72}{0.2} = \frac{72}{2} \times 10 = 360 \text{ Kelvin}$$

If $T_2 = T \Rightarrow T_1 = (T\text{-}60) = 360\text{-}60 = 300$ K

Q4 **At a constant temperature what should be the percentage increase in pressure for 10% decrease in the volume of gas.**

A4 Given 10% decrease in volume of gas.

$P_1V_1=P_2V_2$

$P\times V = P_2\times(0.9V)$ $(P_1 = P)$

$$P_2 = \frac{PV \times 10}{9V}$$

$$P_2 = \frac{10P}{9}$$

$$\text{\% increase in pressure} = \frac{\left(\frac{10P}{9} - P\right)}{P} \times 100 = \frac{100}{9}\%$$

Q5 **A certain amount of H_2 gas occupies a volume of 5 L at 2 atm pressure and 27°C. Now the temperature is changed to 327°C at constant pressure where all H_2 molecules are dissociated into H(g). Calculate the final volume of container**

A5 $H_2(g) \xrightarrow{\quad} 2H(g)$

If x mole dissociates then 2x mole formed (1 : 2)

$$\frac{V_1}{n_1T_1} = \frac{V_2}{n_2T_2} \qquad [\therefore \text{ Pressure is constant, R = constant}]$$

$$\frac{5}{'x'\times 300} = \frac{V_2}{2'x'\times 600}$$

$$V_2 = \frac{5\times '2x'\times 600}{'x'\times 300} = 20\text{ L}$$

$H_2(g) \rightarrow 2H(g)$

Dalton's Law

In a gaseous mixture containing two or more gases, the total pressure of the mixture is equal to the algebraic sum of partial pressure of all gases present. (Gases should be inert to each other).

$P_{Total} = P_{mix}$

$$\left.\begin{matrix} P_A \\ P_B \\ P_C \end{matrix}\right\} \text{Partial pressure of gas}$$

A(g) B(g) C(g)
always homogeneous
mixture

So, $\boxed{P_{Total} = P_A + P_B + P_C}$

Proof :

$P_A.V = n_ART$ ...(1)

$P_BV = n_BRT$ ...(2)

$P_CV = n_CRT$ ...(3)

Also

$P_{Total}V = n_{Total}RT$ ...(4)

On dividing (1) by (4), we get

$$\frac{P_A}{P_{Total}} = \left(\frac{n_A}{n_{Total}}\right)$$

i.e. $P_A = \chi_A.P_{Total}$

Similarly

$P_B = \chi_B P_{Total}$

$P_C = \chi_C P_{Total}$

Now,

$\Rightarrow$ $P_A + P_B + P_C = P_{Total}\ (\chi_A + \chi_B + \chi_C)$

$\Rightarrow$ $= P_A + P_B + P_C = P_{Total}$ as $\chi_A + \chi_B + \chi_C = 1$

Hence proved

So,

$$\boxed{\begin{array}{l}\textbf{In a gaseous mixture}\\ (\textbf{Partial pressure})_{Gas} = (\textbf{Mole Fraction})_{Gas} .P_{Total}\end{array}}$$

ILLUSTRATION:

Q1 **A non–reacting mixture of gases A,B and C is kept into 8.21 litre container at 27°C. If mixture consists 12.5 gm A, 0.5 moles of B and 88 gm of C, then calculate total pressure and partial pressure of each gas in the container. (Molar mass A and C be 25 and 88 g/mol respectively).**

A1 Given:

Mass of gas A = 12.5 gm

Molar Mass of A = 25

Moles of gas A = $\frac{12.5\,g}{25\,g/mol} = 0.5$ mole

Moles of gas B = 0.5 mole

Mass of gas C = 88 gm

Molar mass of gas C = 44 g/mol

Moles of gas C = $\frac{88\,g}{44 g/mol} = 2$ mole

Total moles = (0.5 + 0.5 + 2) mole = 3 mole

$$\text{Using } P_{total} = \frac{n_{Total}.RT}{V} = \frac{3 \times 0.0821 \times 300}{8.21} = 9 \text{ atm}$$

$$\text{i.e. } P_A = \frac{0.5}{3} \times 9 = 1.5 \text{ atm} = P_B$$

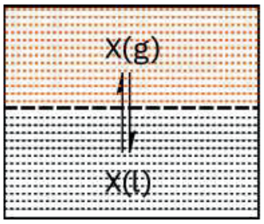
$$= P_B$$

$$P_C = \frac{2}{3} \times 9 = 6 \text{ atm}$$

Vapour pressure of volatile liquid:

At a constant temperature, the pressure exerted by vapour of the substance when an equilibrium is present between liquid and gaseous phases of the substance is known as **vapour pressure of that liquid at that temperature**.

At T Kelvin



At equilibrium

$P_X(g)$ = Vapour pressure of liquid at T Kelvin

- For a particular volatile liquid, the vapour pressure depends upon temperature.

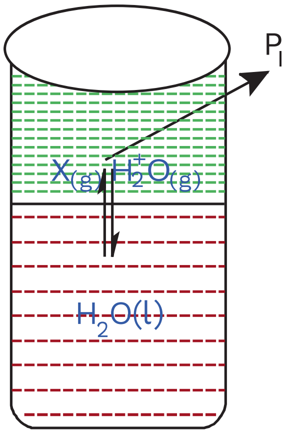
  As. T↑ ⇒ V.P increases

  T ↓ ⇒ V.P decreases

- Vapour pressure of water is also known as aqueous Tension.

  Examples:

  (i) At T Kelvin

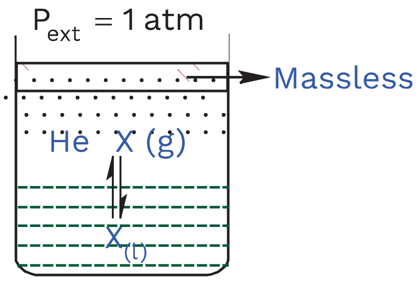


$$P_{Inside} = P_x + P_{H_2O}$$
$$= (P)_x + (V.P)_{H_2O}$$

ILLUSTRATION:

Q1 **To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm, at 0°C) are introduced. Considering the ideal gas behavior, the total volume (in litre) of the gases at 0°C is close to:**

A1 For piston – fitted vessel



$P_{in} = P_{ext}$

$(P_{He} + P_x) \quad = 1\text{atm}$

$\Rightarrow \quad P_{He} \quad = 0.32$ atm

For He

$PV = nRT$

$0.32 \times V = 0.1 \times 22.4$

$V = 7$ L

RELATIVE HUMIDITY (R.H)

- It is a measure of moisture present in the atmosphere.

$$R.H = \left(\frac{P_{H_2O(g)} \text{in atmosphere}}{\text{V.P of } H_2O(l)}\right) \times 100 \text{ at same temperature}$$

ILLUSTRATION:

Q1 **Calculate the weight of water in grams per lite of air at 27°C and 50% relative humidity. Vapour pressure of water at 27°C is 19 mm of Hg.**
(Given R = 0.08 atm – litre / mole – K)

A1 Given Relative humidity = 50%

Vapour pressure of water at 27°C = 19 mm of Hg

$$50 = \frac{P_{H_2O}}{19} \times 100$$

$$P_{H_2O} = \frac{19 \times 50}{100}$$

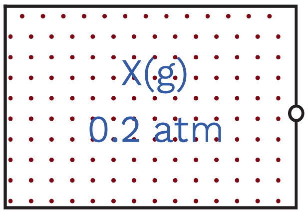
For $H_2O(g)$, $PV = nRT$

$$= \frac{19}{2} \text{mm of Hg}$$

$$\frac{19/2}{760} \times 1 = \frac{w}{18} \times 0.08 \times 300$$

$$= \frac{19 \times 18}{2 \times 760 \times 0.8 \times 300}$$

$$= \frac{3}{320} g$$

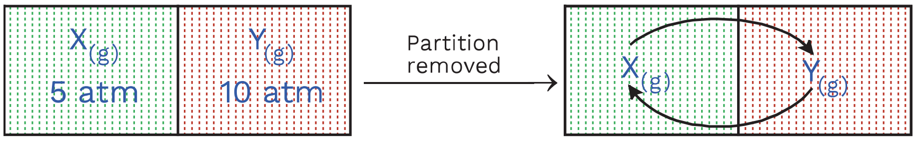


EFFUSION:

The process in which a gas comes out of the vessel through a small opening or hole.

DIFFUSION:

The natural tendency of gases to be intermixed with each other thoroughly.



Homogeneous mixture of X & Y

- Both effusion and diffusion of gas involve travelling of the gas.
- A gas travels due to pressure difference of that gas only.

RATE OF DIFFUSION / EFFUSION (R)

It can be defined as the following:

$$r = \begin{cases} \dfrac{\text{Moles of gas effused}}{\text{Time taken}} \\[2ex] \dfrac{\text{Volume of gas effused}}{\text{Time taken}} \\[2ex] \dfrac{\text{Decrease in pressure}}{\text{Time taken}} \\[2ex] \underline{\text{Distance travelled in narrow tube}} \end{cases}$$

Note: Rate of effusion of a gas is directly proportional to the pressure difference of that gas only.

$(r) \propto (\Delta P)_x$ only

i.e.

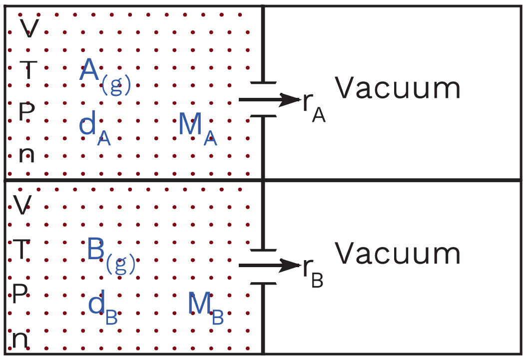
$$(r)_x \propto \left(P_{in} - P_{out}\right)_x$$

Graham’s Law

For different gases, in same conditions of T and P, the rate of effusion of a gas into vacuum is inversely proportional to the square root of the density of the gas.

$$\boxed{\mathbf{r_{gas} \propto \frac{1}{\sqrt{d_{gas}}}}}$$

Case – I : For different gases in similar conditions



$$\because r \propto \frac{1}{\sqrt{d}}$$

$$\Rightarrow \frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$

For a gas,

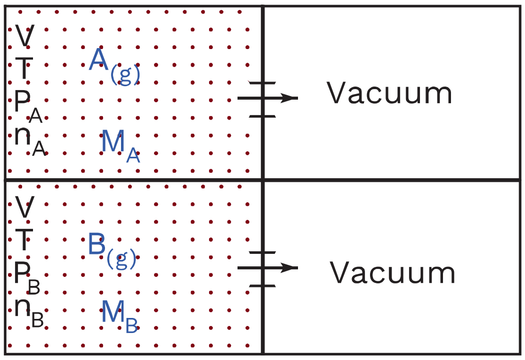
$$PM = dRT$$

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

$d \propto M$ [For same P and T]

$$\text{So, } r \propto \frac{1}{\sqrt{M}} \Rightarrow \quad \frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

CASE – II: FOR DIFFERENT GASES IN DIFFERENT CONDITIONS



$$r_{gas} \propto \frac{1}{\sqrt{M_{gas}}}$$

Also,

$$r_{gas} \propto \left(P_{in} - P_{out}\right)_{Gas}$$

But $P_{out} = 0$

$$r_{Gas} \propto \frac{P_{in}}{\sqrt{M}}$$

$$\Rightarrow \frac{\mathbf{r_A}}{\mathbf{r_B}} = \frac{\mathbf{P_A}}{\mathbf{P_B}}\sqrt{\frac{\mathbf{M_B}}{\mathbf{M_A}}}$$

Also,

$\because P_{inside} \propto n_{inside}$

So, $r \propto \frac{n_{inside}}{\sqrt{M}}$

$$\Rightarrow \frac{\mathbf{r_A}}{\mathbf{r_B}} = \frac{\mathbf{n_A}}{\mathbf{n_B}}\sqrt{\frac{\mathbf{M_B}}{\mathbf{M_A}}}$$

Note: Until given specifically, consider conditions to be identical.

ILLUSTRATION:

Q1 **The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be**

(A) 4 **(B) 2**

(C) 1 **(D) 0.5**

A1 **(B)**

Given: Identical condition of P and T

We know that $r \propto \frac{1}{\sqrt{M}}$ Only

$$\frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{He}}}$$

$$= \sqrt{\frac{16}{4}}$$

$$= \frac{2}{1}$$

$$= 2$$

Or

$$\because\ r = \frac{\text{moles effused}}{\text{time}}$$

So, $\dfrac{r_{He}}{r_{CH_4}} = \dfrac{\left(\dfrac{n_{He} \text{ effused}}{\text{time}}\right)}{\left(\dfrac{n_{CH_4} \text{ effused}}{\text{time}}\right)}$

If time is same

$$\frac{r_{He}}{r_{CH_4}} = \left(\frac{n_{He}}{n_{CH_4}}\right)_{\text{effused}} = \frac{2}{1}$$

i.e. In a given time if one mole CH_4 is effused then in same time 2 mole He will be effused.

Note: Effused molar ratio = Ratio of rates of effusion (In same time)

Q2 **32 ml of He effuses through a fine orifice in 1 minute then what volume of (CH_4 will effuse in 30 seconds under the similar condition.**

A2 Given 32 ml of He effuses through a fine orifice in 1 minute.

$$r \propto \frac{1}{\sqrt{M}} \Rightarrow \frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{He}}} \qquad \left[\therefore r = \frac{V_{\text{effused}}}{\text{time}}\right]$$

$$\Rightarrow \quad \frac{32/60}{V/30} = \sqrt{\frac{16}{4}}$$

$$\Rightarrow \quad \frac{32}{60} \times \frac{30}{V} = \frac{4}{2}$$

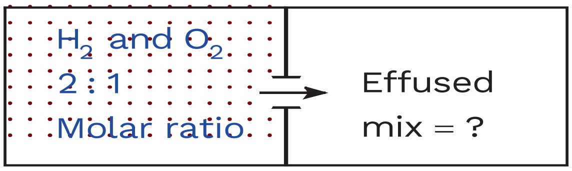
$$\Rightarrow \quad \frac{16}{V} = \frac{4}{2}$$

$$\Rightarrow \quad V = \frac{16 \times 2}{4}$$

$$= 8 \text{ ml}$$

Q3 **A mixture of H_2 and O_2 in 2:1 molar ratio is allowed to effuse through an orifice. Calculate the composition of gases coming out initially.**

A3 We know that



$$r_{gas} \propto \frac{n_{in}}{\sqrt{M}}$$

$$\frac{r_{H_2}}{r_{O_2}} = \left(\frac{n_{H_2}}{n_{O_2}}\right)_{in} \sqrt{\frac{M_{O_2}}{M_{H_2}}}$$

$$= \frac{2}{1} \times \sqrt{\frac{32}{2}}$$

$$= \frac{2}{1} \times \sqrt{16}$$

$$= 2 \times 4$$

$$= \frac{8}{1}$$

A4 **Compare the rate of diffusion for CO and a mixture of He and CH_4 in 3:1 mole ratio under similar condition**

A4 Given:

$$M_{mix} = \frac{3(4) + 1(16)}{3 + 1} = 7\ g / mol$$

We know that

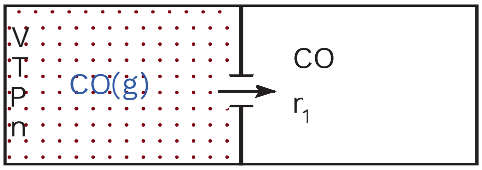
$$r \propto \frac{1}{\sqrt{M}}$$

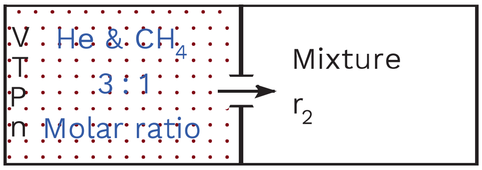
$$\frac{r_{CO}}{r_{mix}} = \sqrt{\frac{M_{mix}}{M_{CO}}}$$

$$= \sqrt{\frac{7}{28}}$$

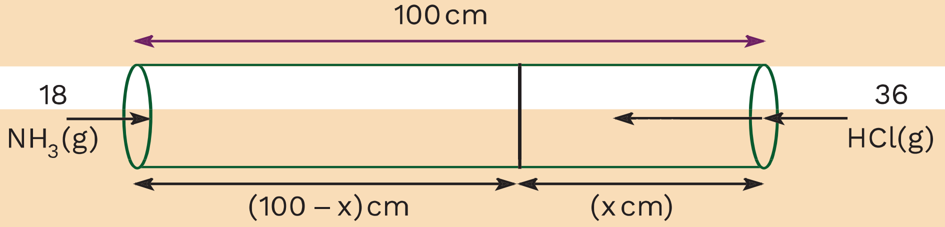
$$= \frac{1}{4}$$

$$= \frac{1}{2}$$





Q5 **Two different bottles containing NH_3(M.M=18) gas and HCl (M.M=36) gas are connected to two ends of a 100 cm long narrow tube. Determine the position of first white ring of NH_4Cl formed, if both bottles are opened simultaneously.**



A5 **When both gases meet first time, first ring of NH_4Cl will be formed.**
Similar conditions (by default)

$$\text{so,} \qquad r \propto \frac{1}{\sqrt{M}} \text{ only}$$

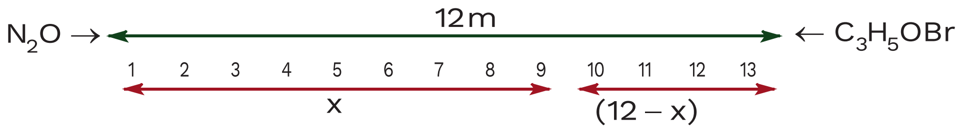
$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$

$$\Rightarrow 2x = 10 - x$$

$$\Rightarrow x = \frac{100}{\sqrt{2+1}}$$

Q6 **A classroom consist 13 equidistant rows of benches. From first bench the teacher releases, laughing gas (N_2O) and simultaneously the student from last bench releases weeping gas (C_3H_5OBr). Calculate at which bench students will laugh and weep simultaneously?**

A7



$$\frac{x/t}{(12-x)/t} = \sqrt{\frac{137}{44}} \approx 1.7$$

$$\Rightarrow \quad x = 1.7(12-x)$$

$$x = 20.4 - 1.7x$$

$$\Rightarrow x + 1.7x = 20.4$$

$$2.7x = 20.4$$

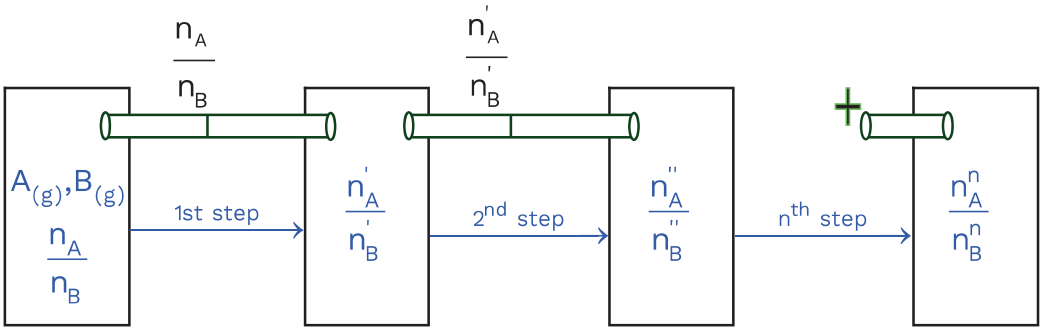
$$\Rightarrow \quad x = \frac{20.4}{2.7}$$

$$\Rightarrow \quad x = 7.55$$

$$\Rightarrow \quad x = 8\,\text{m}$$ **i.e., 9th bench from first**

Kinetic Theory of Gases

Note: Successive effusion



$\because$ Effused molar ratio =ratio of rates

Also $r \propto \frac{(n)_{\text{intial}}}{\sqrt{M}}$

In any step,

$$\frac{(n_A)}{(n_B)}_{\text{effused}} = \left(\frac{n_A}{n_B}\right)_{\text{Inside}} \sqrt{\frac{M_B}{M_A}}$$

1st step
$$\frac{n'_A}{n'_B} = \frac{n_A}{n_B}\left(\sqrt{\frac{M_B}{M_A}}\right)$$

2nd step
$$\frac{n''_A}{n''_B} = \frac{n'_A}{n'_B}\sqrt{\frac{M_B}{M_A}}$$

$$\frac{n''_A}{n''_B} = \frac{n_A}{n_B}\left(\sqrt{\frac{M_B}{M_A}}\right)^2$$

So, nth step :

$$\frac{n^n_A}{n^n_B} = \frac{n_A}{n_B}\left(\sqrt{\frac{M_B}{M_A}}\right)^n$$

Effused ratio after 'n' steps

$$\boxed{\left(\frac{n''_A}{n''_B}\right) = \frac{n_A}{n_B}\left(\sqrt{\frac{M_B}{M_A}}\right)^n}$$

No of steps

Initial ratio

ILLUSTRATION:

Q1 **A mixture of H_2 and N_2 gases in 1:14 molar ratio is being separated by successive effusion. Calculate after how many steps the molar ratio becomes 14:1?**

A1 **Given** :

Mixture of H_2 and N_2 gases in 1:14 molar ratio.

$$\left(\frac{n_{H_2}}{n_{N_2}}\right)_{\text{Effusion}} = \left(\frac{n_{H_2}}{n_{N_2}}\right)_{\text{Initial}} \left(\sqrt{\frac{M_{N_2}}{M_{H_2}}}\right)$$

$$\frac{14}{1} = \frac{1}{14}\left(\sqrt{\frac{28}{2}}\right)^n$$

$$(14)^2 = (14)^{n/2}$$

$$\Rightarrow \ n = 4$$

KINETIC THEORY OF GASES:

- Applicable only and only for ideal gases.
- **Main postulates of Kinetic theory of gases are as following:**

i) A gas is the collection of very large number of particles (Bulk amount).
ii) Volume of particle is negligible as compared to volume of container.
iii) There is no force of attraction between the particles of a gas at ordinary temperature and pressure.
iv) All particles travel in straight line with high speed and continuously stroke with walls of container.
v) All collisions are perfectly elastic. Hence no change in total kinetic energy of gas particles.
vi) The average kinetic energy per molecule depends upon temperature only.
vii) The pressure of gas is due to collisions by particles with walls of container.

As per kinetic theory of gases, the pressure exerted by one particle of mass ‘m’ in a container of volume ‘V’ is given as following: (u– speed of particle)

$$\boxed{P = \frac{1}{3}\frac{mu^2}{V}}$$

- For a gas sample containing ‘N’ particles in a container of volume ‘V’ and having speeds u_1, u_2, u_3 .... u_n,

$$P = \frac{1}{3}\frac{m}{V}\left[u_1^2 + u_2^2 + u_3^2 + \text{..........}u_n^2\right]$$

$$P = \frac{1}{3}\frac{m}{V}\left[N.\ u_{rms}^2\right]$$

- For one mole gas

  i.e. $N = N_A$

  So, $\mathbf{P = \frac{1}{3}\frac{m}{V}.N_A u_{rms}^2}$

  Where 'm' is mass of one particle.

  (mN_A) is mass of N_A particles or molar mass of gas (M).

  So, $\mathbf{P = \frac{1}{3}\frac{M}{V}u_{rms}^2}$

CALCULATION OF K.E:

For one particle,

$$K.E = \frac{1}{2}m.u^2$$

For gas sample containing 'N' particles:

$$K.E = \frac{1}{2}m.\left(u_1^2 + u_2^2 + \text{...................}u_n^2\right)$$

$$= \frac{1}{2}m\left(Nu_{rms}^2\right)$$

For 1 mole gas

$$K.E = \frac{1}{2}mN_A u_{rms}^2$$

$$K.E = \frac{1}{2}Mu_{rms}^2$$

$$K.E = \frac{1}{2}(3PV)$$

$$(K.E)_{1mole} = \frac{3}{2}PV \qquad [\because n = 1]$$

$$(K.E)_{1mole} = \frac{3}{2}RT$$

For 'n' mole gas

$$(K.E)_{Total} = \frac{3}{2}nRT$$

$$(K.E)_{Total} \propto (n)_{gas}$$

$$(K.E)_{Total} \propto T(\text{Kelvin})$$

AVERAGE K.E PER MOLECULE:

$$(K.E)_{avg.} = \frac{\text{Total K.E}}{\text{No. of molecule}}$$

$$(K.E)_{avg.} = \frac{\frac{3}{2}n.R.T}{n.N_A}$$

$$(K.E)_{avg} = \frac{3}{2}k.T$$

$$(K.E)_{avg} \propto T_{(Kelvin)} \text{ only}$$

Also:

k is Boltzmann's constant

$$k = \left(\frac{R}{N_A}\right)$$

$$k = \frac{8.314 J/mol/K}{6.02 \times 10^{23} mol^{-1}}$$

$k = 1.38 \times 10^{-23}$ J/K

ILLUSTRATION:

Q1 **As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor:**

(A) $\frac{1}{2}$ **(B) $\sqrt{\frac{313}{293}}$** **(C) $\frac{313}{293}$** **(D) 2**

A1 (C)

Temperature is raised from

20°C to 40°C

We know that

$(K.E)_{avg} \propto T(Kelvin)$

$$\frac{K.E_f}{K.E_i} = \frac{313}{293}$$

Q2 **Two flasks A and B have equal volumes, A is maintained at 300 K and B at 600 K, while A contains H_2 gas, B has an equal mass of CO_2 gas. Find the ratio of total to translational kinetic energy of gases in flaks A to that of B.**

(A) 1:2 **(B) 11:1** **(C) 33:2** **(D) 55:7**

A2 A is maintained at 300 K and B is at 600 K. A contains H_2 gas and B has mass equal mass of CO_2 gas

We know that $(K.E)_{Total} \propto n.T$

$$\frac{(K.E)_A}{(K.E)_B} = \frac{n_{H_2} \times 300}{n_{CO_2} \times 600}$$

$$\frac{(K.E)_A}{(K.E)_B} = \frac{w/2}{w/44} \times \frac{1}{2}$$

$$\frac{(K.E)_A}{(K.E)_B} = \frac{44}{2} \times \frac{1}{2}$$

$$\frac{(K.E)_A}{(K.E)_B} = \frac{11}{1}$$

DIFFERENT SPEEDS OF A GAS

For a gas sample containing 'N' particles having speeds u_1, u_2, u_3 .... u_N, there are following three types of speeds.

i) Average / Mean speed (u_{avg})

$$u_{avg} = \frac{u_1 + u_2 + u_3 + \text{..........} u_n}{N}$$

$$u_{avg} = \sqrt{\frac{\sum_{i=1}^{N} u_i^e}{N}}$$

ii) Root mean square speed (u_{rms})

$$u_{rms} = \frac{\sum_{i=1}^{N} u_i^2}{N}$$

$$u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 \text{.........} u_N^2}{N}}$$

$$u_{rms}^2.N = \left(u_1^2 + u_2^2 + \text{..........} u_n^2\right)$$

iii) Most probable speed (u_{mp})

The speed corresponding to maximum number of particles.

Let 6×10^3 particles have 10 m/s

1×10^5 particles have 2 m/s

4×10^2 partciles = 12 m/s

So,

$u_{mp} = 2m/s$

For ‘n’ mole gas

$$\mathbf{u_{rms}} = \sqrt{\frac{\mathbf{3RT}}{\mathbf{M}}} = \sqrt{\frac{\mathbf{3PV}}{\mathbf{n.M}}} = \sqrt{\frac{\mathbf{3P}}{\mathbf{d}}}$$

$$\mathbf{u_{avg}} = \sqrt{\frac{\mathbf{8RT}}{\pi\mathbf{M}}} = \sqrt{\frac{\mathbf{8PV}}{\pi\mathbf{nM}}} = \sqrt{\frac{\mathbf{8P}}{\pi\mathbf{d}}}$$

$$\mathbf{u_{mp}} = \sqrt{\frac{\mathbf{2RT}}{\mathbf{M}}} = \sqrt{\frac{\mathbf{2PV}}{\mathbf{nM}}} = \sqrt{\frac{\mathbf{2P}}{\mathbf{d}}}$$

Note: In above relations put all values in S.I units only.

R = 8.314 J/mol.K

T in Kelvin

P in N/m^2 or Pascal

V = Volume of container (in m^3)

d = density of gas (in kg/m^3)

n = moles of gas

M = Molar mass of gas (kg/mol)

For a particular gas at constant temperature:

$$u_{rms} : u_{avg} : u_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$$

$$= 1.73 : 1.62 : 1.41$$

i.e., $U_{rms} > u_{avg} > u_{mp}$

ILLUSTRATION:

Q1 **The ratio between the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is:**

(A) 4 **(B) 2** **(C) 1** **(D) $\frac{1}{4}$**

A1 (C)

We know that: $u_{rms} \propto \sqrt{\frac{T}{M}} = u_{rms} \propto \frac{T}{M}$

$$\frac{u_{H_2}}{u_{O_2}} = \sqrt{\frac{50/2\times10^{-3}}{800/32\times10^{-3}}}$$

$$\frac{u_{H_2}}{u_{O_2}} = \sqrt{\frac{50\times32}{800\times2}}$$

$$\frac{u_{H_2}}{u_{O_2}} = 1$$

Q2 **At 400 K, the root mean square (rms) speed of a gas ‘x’ (molecular weight = 40) is equal to the most probable speed of gas y at 60 K. The molecular weight of gas y is:**

A2 At 400 K, rms of gas x is equal to most probable speed of gas y at 60K.

$$(u_{rms})_x = (u_{MP})_y$$

$$\left(\sqrt{\frac{3RT}{M}}\right)_x = \left(\sqrt{\frac{2RT}{M}}\right)_y$$

i.e. $$\frac{3\times400}{40} = \frac{2\times60}{M}$$

$$\Rightarrow \quad \frac{1}{M} = \frac{3\times400}{40\times2\times60}$$

$$\Rightarrow \quad \frac{1}{M} = \frac{1}{4}$$

$\Rightarrow$ $M = 4$

$\therefore$ Molar mass of gas y = 4

Q3 **Which of the following statements is/are correct regarding the root mean square speed (u_{rms}) and average translational K.E (E_{av}) of a molecule in a gas at equilibrium.**

(A) U_{rms} is doubled when its temperature is increased four times

(B) U_{rms} is inversely proportional to the square root of its molecular mass

(C) E_{av} at a given temperature does not depend on its molecular mass

(D) E_{av} is doubled when its temperature is increased four times

A3 A,B,C

Relation of U_{rms} and E_{av}

$$E_{av} = \frac{3}{2}RT, \qquad U_{rms} = \sqrt{\frac{3RT}{M}}$$

$$U_{rms} \propto \frac{1}{\sqrt{M}}$$

E_{av} does not depend on its molecular mass.

According to the relation given above E_{av} get doubled when the temperature is increased 2 times. Thus option (D) is incorrect.

∴ Statements A , B and C are correct regarding the root mean square speed (U_{rms}) and average translational kinetic energy (E_{av}) of a molecule if gas at equilibrium.

Maxwell's distribution of molecular speeds

- In a gas sample, at a certain temperature all particles do not have same speed but they posses a wide range of molecular speed.

  i.e., At T Kelvin

- According to Maxwell, in a gas sample at a certain temperature, the number of particles corresponding to a particular speed remains constant which can be given by following equation:

$$\frac{dN}{du} = 4\sqrt{\pi}N\left(\frac{M}{2RT}\right)^{\frac{3}{2}}\left(e^{-\frac{Mu^2}{2RT}}\right)u^2$$

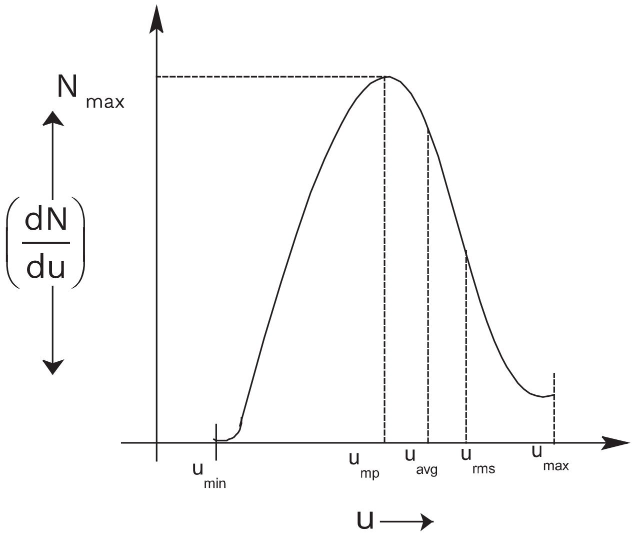
where:

$$\left.\begin{array}{l} N = \text{Total number of particles in gas sample} \\ M = \text{Molar mass of gas} \\ R = \text{Gas constant} \\ T = \text{Temperature} \\ u = \text{Speed} \end{array}\right\} \text{All in SI units}$$

$$\frac{dN}{du} = \text{No. of particles corresponding to speed 'u'.}$$

$$\text{Also } \frac{\left(\frac{dN}{du}\right)}{N} = \text{Fraction of particles corresponding to speed 'u'}$$

For a particular gas at a certain temperature:



- At any speed, the height of the curve represents no. of particles corresponding to that speed.
- So, the peak represents maximum number of particles and hence the corresponding speed is u_{mp}

For N_{max}, put $u = u_{mp}$ in the equation, if $u = u_{mp} = \sqrt{\frac{2RT}{M}}$

$$\left(\frac{dN}{du}\right) \Rightarrow N_{max} = 4\sqrt{\pi}N\left(\frac{M}{2RT}\right)^{\frac{3}{2}} e^{-\frac{M}{2RT}\times\frac{2RT}{M}}\left(\frac{2RT}{M}\right)$$

$$\boxed{\mathbf{N_{max} = \frac{4\sqrt{\pi}N}{e}\left(\frac{M}{2RT}\right)^{\frac{1}{2}}}}$$

- In a gas sample, particles having very low and very high speeds are very less means most particles have speeds near to u_{mp}.
- Total area under the curve =N

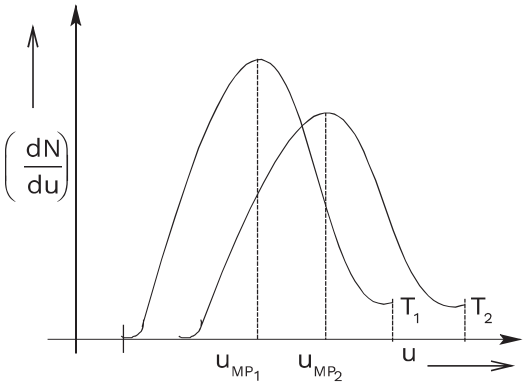
> **Note:** If $\left(\frac{dN}{du}\right)$ is taken on y-axis, area under the curve=1 (sum of fraction)

CASE 1 : FOR SAME GAS AT DIFFERENT TEMPERATURES

On increasing temperature, the curve become broader and vice-versa with same area under the curve.

$$u_{mp} \propto \sqrt{T}$$

$$N_{max} \propto \frac{1}{\sqrt{T}}$$



CASE 2 : FOR DIFFERENT GASES AT SAME TEMPERATURE

If molar mass is more then curve becomes steeper and vice-versa with same number of particles.

$$U_{mp} \propto \frac{1}{\sqrt{M}}$$

$$N_{max} \propto \sqrt{M}$$

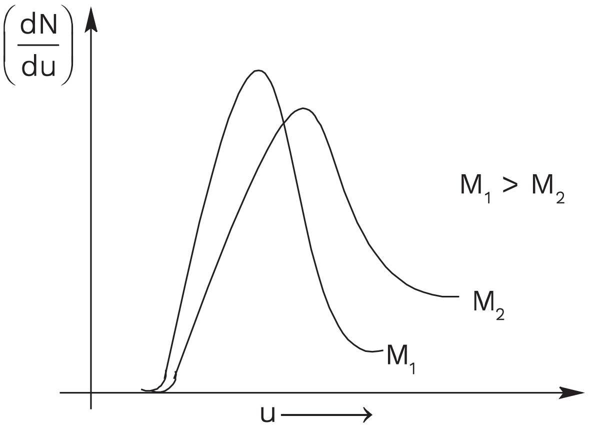


ILLUSTRATION:

Q1 **According to kinetic theory of gases:**

(A) Collisions are always elastic

(B) Heavier molecules transfer more momentum to the wall of the container.

(C) Only a small number of molecules have very high velocity.

(D) Between collisions, the molecules move in straight lines with constant velocities.

A1 **A,C,D**

Theory Based

Q2 **Which one of the following statements is NOT true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?**

(A) The fraction of the molecules with the most probable speed increases.

(B) The most probable speed increases

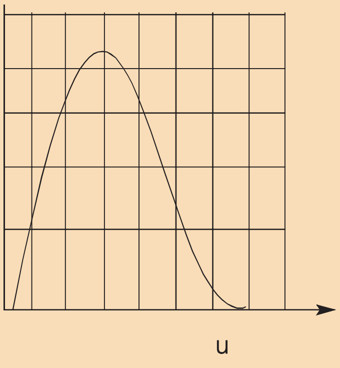
(C) The area under the distribution curve remains the same as under the lower temperature.

(D) The distribution becomes broader.

A2 **A**

The fraction of the molecules with the most probable speed decreases.

Q3 **If the distribution of molecular speeds of a gas is as per the figure shown below, then the ratio of the most probable, the average and the root mean square speed respectively is**



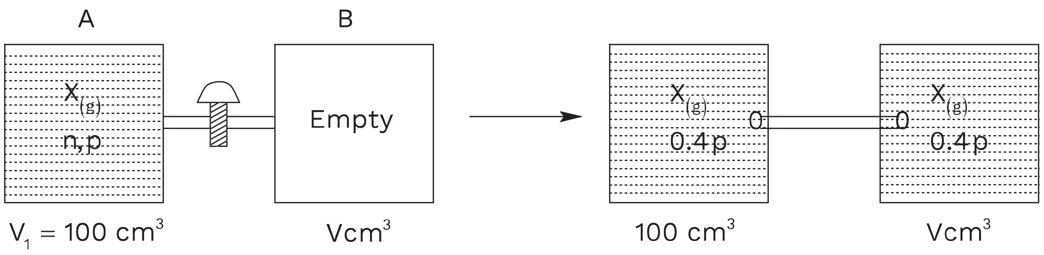
(A) 1 : 1 : 1 **(B) 1 : 1 : 1.224** **(C) 1 : 1.128 : 1.224** **(D)1 : 1.128 : 1**

A3 (B) 1 : 1 : 1.224

Graph represents symmetrical distribution of speed and hence, the most probable and the average speed should be same, but the root mean square speed must be greater than the average speed.

Q4 **Two glass bulbs A and B are connected by a very small tube having a stopcock. Bulb A has a volume of 100 cm³ and on contained the gas, while bulb B was empty before opening the stopcock. The pressure fell down to 40% at constant temperature in container A. Calculate volume of the bulb B(in cm³).**

A4



For X(g), $PV = nRT$

So, $P_1V_1 = P_2V_2$

$(n, R, T \text{ are constant})$

$$P \times 100 = 0.4P(100 + V)$$

$$P \times 100 = 40P + 0.4PV$$

$$100P - 40P = 0.4PV$$

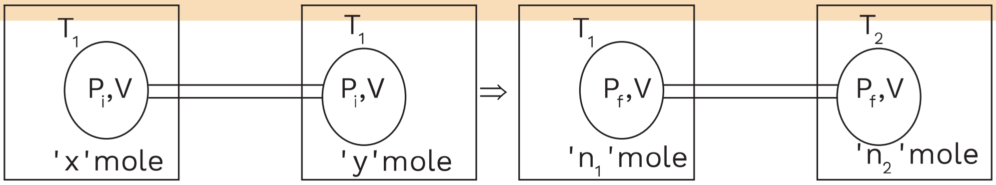
$$60P = 0.4PV$$

$$\Rightarrow \quad V = \frac{60P}{0.4P}$$

$$= \frac{60}{4} \times 10$$

$\Rightarrow$ Volume of Bulb B = 150 cm^3

Q5 **Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure P_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure P_f is:**



(A) $2P_i\left(\frac{T_1T_2}{T_1+T_2}\right)$ **(B)** $P_i\left(\frac{T_1T_2}{T_1+T_2}\right)$ **(C)** $2P_i\left(\frac{T_1}{T_1+T_2}\right)$ **(D)** $2P_i\left(\frac{T_2}{T_1+T_2}\right)$

A5 (D)

Initially

Let 'x' moles of gas in first bulbs $x = \frac{P_iV}{RT_1}$

and 'y' moles of gas in bulb second, $y = \frac{P_iV}{RT_1}$

After the temperature of second bulb is raised to T_2, then the number of moles of gas in both the bulbs are:

$$n_1 = \frac{P_fV}{RT_1} \text{ and } n_2 = \frac{P_fV}{RT_2}$$

Total no. of moles of gas in both bulbs remains same in both the cases.

$$x + y = n_1 + n_2$$

$$\frac{2P_iV}{RT_1} = \frac{P_fV}{RT_1} + \frac{P_fV}{RT_2}$$

$$\frac{2P_iV}{RT_1} = \frac{P_fV}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$$

$$\frac{2P_iV}{RT_1} = \frac{P_fV}{R}\left(\frac{T_2+T_1}{T_1T_2}\right)$$

$$\Rightarrow P_f = \frac{2P_iV}{RT_1} \times \frac{R}{V}\left(\frac{T_1T_2}{T_2+T_1}\right)$$

$$P_f = \frac{2P_iT_2}{T_1+T_2}$$

Hence, option (D) is correct.

Q6 A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does NOT allow the gas to leak across (Figure 2), the volume (in m^3) of the compartment A after the system attains equilibrium is:

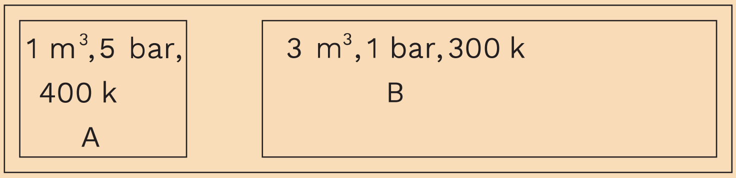


Figure A

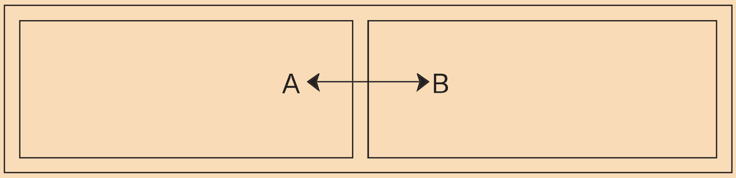


Figure B

A6 For compartment A, $V_i = 1\ m^3$, $P_i = 5$ bar, $T_1 = 400$ k. Let $V_f = y\ m^3$, $P_f = P$, $T_f = T$

. 'n' is constant.

So: $\frac{P_iV_i}{RT_i} = \frac{P_fV_f}{RT_f}$

$$\Rightarrow \frac{5 \times 1}{400} = \frac{P \times y}{T}$$

$$\Rightarrow \frac{P}{T} = \frac{5}{400\,y} \ldots.(1)$$

For compartment B:

$P_i = 1$ bar, $V_i = 3m^3$, $T_i = 300$ k

Let $P_f' = P, V_f' = (3 - y)m^3, T_f' = T$

$n_i = P_f$

$$\frac{P_f'V_f'}{RT_f'} = \frac{P_f'V_f'}{R_fT_f'}$$

$$\frac{1 \times 3}{300} = \frac{P \times (3 - y)}{T}$$

$$\frac{3}{300} \times \frac{1}{(3 - y)} = \frac{P}{T}$$

$$\Rightarrow \frac{P}{T} = \frac{3}{300} \times \frac{1}{3 - y} \ldots\ldots(2)$$

On comparing (1) & (2) we get

$$\Rightarrow \frac{3}{300} \times \frac{1}{(3 - y)} = \frac{5}{400y}$$

$$\Rightarrow \frac{3}{300} \times \frac{400}{5} = \frac{3 - y}{y}$$

$$\frac{4}{5} = \frac{3 - y}{y}$$

$$\Rightarrow 4y = 5(3 - y)$$

$$4y = 15 - 5y$$

$$\Rightarrow 9y = 15$$

$$\Rightarrow y = \frac{15}{9}\ \text{m}^3$$

$$\Rightarrow y = 1.67\ \text{m}^3$$

Collision Parameter

In a gas sample, since particle collide continuously with each other so there are some properties related to these collisions.

i) **Z_1 (Collision frequency)**

The average number of collisions made by one particle per unit time, per unit volume.

For a gas,

$$Z_1 = \sqrt{2}\pi\sigma^2 u_{avg}.N^*$$

where: σ is collision diameter $(\sigma = 2r)$

$$u_{avg} = \sqrt{\frac{8RT}{\pi M}}$$

$N^* =$ no. of particles per unit volume $\left(\frac{N}{V}\right)$

Since, $PV = nRT$

$$PV = \frac{N}{N_A}.R.T$$

$$PV = N.k.T$$

$$\Rightarrow \left(\frac{N}{V}\right) = N^* = \frac{P}{k.T}$$

ii) **Z_{11} [Collision frequency (or Z_{AA})]**

The average number of biomolecular collision (between two particles) for same gas per unit-time, per unit volume.

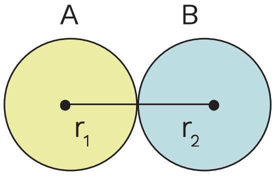
For a gas,

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2\ u_{avg}N^*$$

i.e. $Z_{11} = \frac{1}{2}Z_1N^*$

iii) **Z_{12} or Z_{AB} (Collision frequency)**

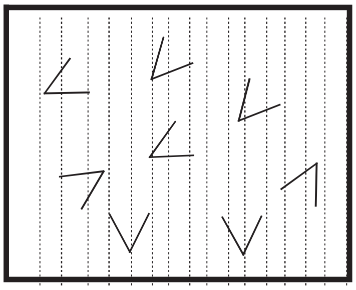
The average no. of bimolecular collisions between particles of different gases per unit time, per unit volume.



$\Rightarrow \sigma = (r_1 + r_2)$

MEAN FREE PATH (λ)

The average distance travelled by particle between two successive collisions.



Average of such distances= λ

For a gas:

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 . N^*}$$

NOTE:

If collision frequency is more, then distance travelled will be lesser $\left(\text{less}\,\lambda\right)$ and vice versa.

EFFECT OF T AND P

$$Z_1 \propto \sqrt{T} . \frac{P}{T}$$

$$\boxed{Z_1 \propto \frac{P}{\sqrt{T}}}$$

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

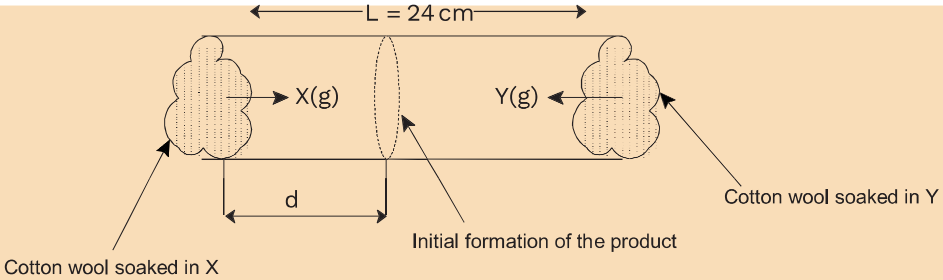
$$\boxed{Z_{11} \propto \frac{P^2}{T^{\frac{3}{2}}}}$$

$$\lambda \propto \frac{1}{\left(\frac{P}{T}\right)}$$

$$\boxed{\lambda \propto \frac{T}{P}}$$

ILLUSTRATION:

Q1 **'X' and 'Y' are two volatile liquids with molar weights of $10\,g\,mol^{-1}$ and $40\,g\,mol^{-1}$ respectively. Two cotton plugs, one soaked in 'X' and other soaked in 'Y', are simultaneously placed at the ends of a tube of length 'L' (24cm), as shown in the figure. The tube is filled with an inert gas at 1 atm pressure and a temperature of 300 K. Vapours 'X' and 'Y' react to form a product which is first observed at distance 'd' cm from the plug soaked in X. Take X and Y to have molecular diameters and assume ideal behaviour for the inert gas and the two vapours.**



The value of d (in cm) shown in figure, as estimated from Graham's law, is:

(A) 8 **(B) 12** **(C) 16** **(D) 20**

A1 As:

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

$$\frac{r_x}{r_y} = \sqrt{\frac{M_y}{M_x}}$$

$$\frac{d/t}{(24-d)/t} = \sqrt{\frac{40}{10}}$$

$$\Rightarrow d = 2(24-d)$$

$$\Rightarrow d = 16 \text{ cm}$$

Q2 **The experimental value of 'd' is found to be smaller than the estimate obtained using Graham's law. This is due to:**

(A) Larger mean free path for X as compared to that of Y.

(B) Larger mean free path for Y as compared to that of X.

(C) Increased collision frequency of Y with the inert gas as compared to that of X with the inert gas.

(D) Increased collision frequency of X with inert gas as compared to that of Y with the inert gas.

A2 **(D)**

With increase in collision frequency, the molecular speed decreases than the expected so the distance covered will be less.

Q3 **The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increase x times, then value of 'x' is:**

Given: diffusion coefficient $\mu \propto \lambda$

A3 **Also,** $\mu \propto u_{avg}$

$$\Rightarrow \mu \propto \lambda u_{avg}$$

$$\Rightarrow \mu \propto \left(\frac{T}{P}\right)\left(\sqrt{T}\right)$$

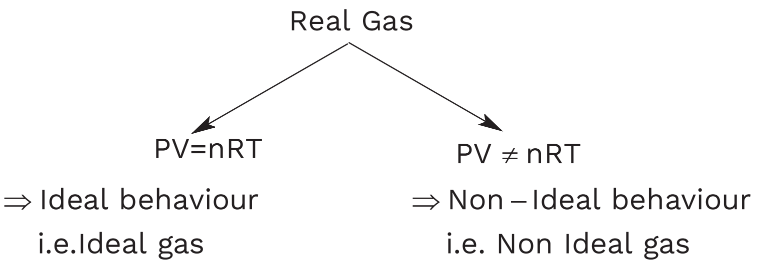
$$\Rightarrow \mu \propto \frac{T^{\frac{3}{2}}}{P}$$

$$\Rightarrow \frac{\mu_2}{\mu_1} = \left(\frac{T_2}{T_1}\right)^{\frac{3}{2}}\left(\frac{P_1}{P_2}\right)$$

$$\therefore \frac{\mu_2}{\mu_1} = \left(\frac{4}{1}\right)^{\frac{3}{2}}\left(\frac{1}{2}\right) = 4$$

REAL GASES:

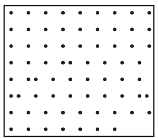
- No gas is always ideal means all are real gases which just can show ideal behaviour under certain conditions.



- For real gas: -
  (i) Volume of gas particles is not negligible as compared to volume of container.
  (ii) Intermolecular forces are present (Both attractive and repulsive forces).
- Due to above reasons there are some changes (corrections) in pressure of gas and free

volume of gas, which are as following: -

- **Volume Correction (V')**
  - Free volume of gas:
    The volume available for gas particles to move freely (V_{gas}).



Let volume of container is V

For an ideal gas volume of particles ⟶ Negligible

$$\Rightarrow \boxed{\left(V_{gas}\right)\text{ideal} = V}$$

but for a real gas

$$\left(V_{gas}\right)_{Real} < V$$

$$\boxed{V_{gas} = V - V'}$$

Where V' is effective volume of gas particles.

For a gas:

$b \rightarrow$ effective volume of 1 mole particles

So for n-mole gas:

Effective volume $\left(V'\right) = nb$

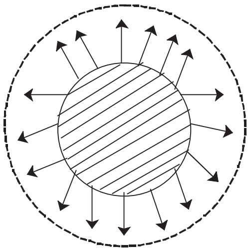
$$V_{gas} = V - nb$$

Where V_{gas} is free volume

'nb' is effective volume of particles.

'V' is volume of container

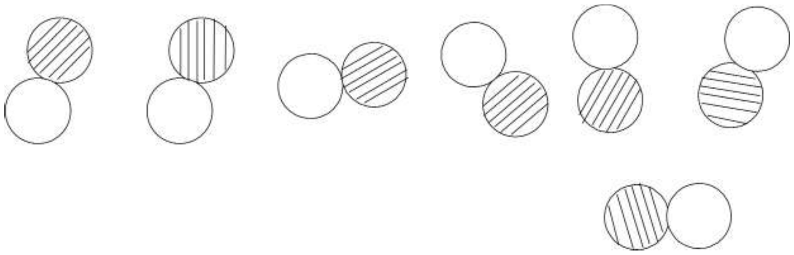
- Since gas particles collide continuously with very high frequency (10^6 per sec), they acquire some extra volume around themselves in which no other particle can enter.



- So the actual volume of particle and this extra acquired volume are collectively known as effective volume.

CALCULATION OF ‘b’

- Gas particles continuously collide with each other in which bimolecular collisions are maximum $\left(\sim 99\%\right)$.
- So due to high collision frequency particles appear as pairs.



- If all above collisions are superimposed with common centre of mass, then a sphere is formed which will contain, all these collisions.

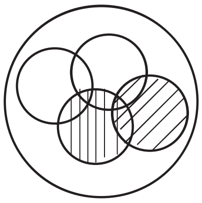
If radius of particle = r

$\Rightarrow$ radius of sphere =m 2r

In this sphere, since no other particle can enter, so effective volume of 2 particles

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

$$= 8.\frac{4}{3}\pi r^3$$



Effective volume of one particle $= 4.\frac{4}{3}\pi r^3$

So, for b (1 mole = N_A Particle)

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

NOTE: FOR A GAS

(Effective volume = $4 \times$ actual volume of particle)

ILLUSTRATION:

Q1 **The density of mercury is 13.6 g/cm^3. Estimate the 'b' value of Hg(g). (Atomic mass of Hg = 200).**

A1 58.82 cm^3

Given: density of mercury = 13.6 g/cm^3

'b' is effective volume of one mole particles.

Mass of 1 mole Hg = 200 grams

$$\text{Volume of 1 mole Hg(l)} = \frac{200}{13.6}\ \text{cm}^3$$

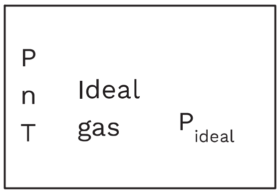
$$= \text{actual volume of 1 mole particles.}$$

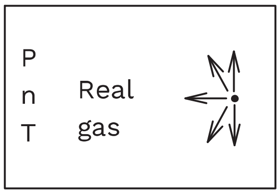
$$\text{Effective volume} = 4 \times \text{actual value of particles}$$

$$b = 4 \times \frac{200}{13.6}\,\text{cm}^3 = 58.82\ \text{cm}^3$$

PRESSURE CORRECTION (P')

- The pressure of a gas is due to collisions by particles with walls of container.





- There are no forces among particles of an ideal gas, so its particles strike on the wall with same speed as they possess.

  But in a real gas, the particle which is going to strike on the wall is being attracted by other particles. Hence it will strike on the wall with lesser speed as compared to an ideal gas under similar conditions.
- Hence the pressure exerted by a real gas in similar conditions of n, V and T is lesser as compared to an ideal gas.

IN SIMILAR CONDITIONS

$$\boxed{P_{gas} = P_{ideal} - P'}$$

where P_{gas} = Pressure of gas, P_{ideal} = Pressure of ideal gas, P′ = Pressure correction

FOR A REAL GAS,

$$P' = \frac{an^2}{V^2}$$

$$\Rightarrow \boxed{P_{gas} = P_{ideal} - \frac{an^2}{V^2}}$$

where, n = moles of gas, V = volume of container, a = (+) constant for gas

VANDER WAAL EQUATION

- To describe behaviour of a real gas, many equations were proposed out of them, most used equation is Vander Waal equation which is as following:

For ‘n’ mole,

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

For 1 mole,

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

Where P is pressure of gas

volume of container (V_m = volume for 1 mole gas)

n = moles of gas

R = 0.0821 L atm/mole.K

T = Kelvin temperature

a, b = Vander Waal constant for gas

NOTE: For a particular gas, a and b have certain fixed values.

CONSTANT ‘a’

- For a gas ‘a’ is the measure of intermolecular attractive forces (IMAF).

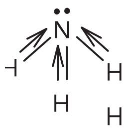
$$\boxed{\text{More IMAF} \Rightarrow \text{More value of } (a)}$$

$$\boxed{\text{Less IMAF} \Rightarrow \text{Less value of 'a'}}$$

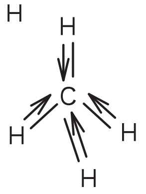
e.g.

$H_2 \Rightarrow H \overset{\odot}{—} H$ Non polar molecule

$HCl \Rightarrow \overset{\delta+}{H} \overset{\odot}{—} \overset{\delta-}{Cl}$ Polar molecule



Vector addition $\neq 0 \Rightarrow$ polar molecule



Vector addition $= 0 \Rightarrow$ Non – polar molecule

Types of molecule	**IMAF**
Polar	Dipole-dipole (Strong)
Non Polar	London Forces (Weak)

London < dipole –dipole < H -bonding

If type of IMAF is same then,

|IMAF| $\propto$ Size of molecule → (surface area)

e.g. H_2 (non polar) and CO_2 (Non polar)

London forces exist in both but size of CO_2 is greater than size of H_2.

$$\Rightarrow \left|IMAF\right|_{CO_2} > \left|IMAF\right|_{H_2}$$

i.e. $(a)_{CO_2} > (a)_{H_2}$

CONSTANT ‘b’

For a gas, ‘b’ is the measure of size of molecule.

More molecular size ⇒ More value of ‘b’.

Less molecular size ⇒ Less value of ‘b’

$$\text{Since } b = 4.\frac{4}{3}\pi r^3.N_A$$

$$b \propto r^3$$

UNITS OF a AND b

$$P = \frac{an^2}{V^2} \qquad \Rightarrow \qquad a = \frac{PV^2}{n^2}$$

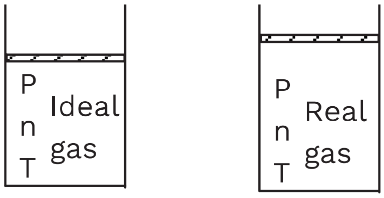
i.e. $a = \text{atm.L}^2.\text{mol}^{-2}$

$V = nb \Rightarrow b = V/n$

i.e. $b = \text{L mol}^{-1}$

COMPRESSIBILITY FACTOR (Z)

It gives information about the behaviour of a gas in given conditions.



$V_{container} = V_{ideal}$ $\qquad$ $V_{container} \neq V_{Real}$

$$\boxed{(Z)_{Real} = \frac{V_{Real}}{V_{Ideal}}}$$

- For ideal

$P.V_{ideal} = nRT$

$$(Z)_{Real} = V_{Real} \,/\, (nRT/P) = = \frac{PV_{real}}{nRT}$$

$$\boxed{Z = \frac{PV}{nRT} = \frac{PV_m}{RT} = \frac{PM}{dRT} = \frac{P}{CRT}}$$

Where

P is pressure of gas

V, V_m is volume of container (l)

n is mole of gas

R = 0.0821 L atm/mol.K

T = Kelvin Temperature

M = Molar mass (g/mol)

d = density (g/L)

C = Molarity of gas (Mol/L)

Compressibility factor & Related Graphs

- The value of Z gives information about the behaviour of gas as following:-

  If $Z = 1 \Rightarrow$ $PV = nRT$ i.e. Ideal behaviour

  Also, $V_{Real} = V_{Ideal}$

  i.e. Both attractive and repulsive forces are mutually balanced with each other ($F_{net} = 0$).

  If $\boxed{\text{If } Z \neq 1}$ then $PV \neq nRT \Rightarrow$ Non-Ideal behaviour

$\boxed{Z < 1}$	$\boxed{Z > 1}$
$V_{Real} < V_{Ideal}$	$V_{Real} > V_{ideal}$
i.e. Attractive forces dominantes.	i.e. Repulsive force dominantes
(-ve deviation from ideal behaviour)	(+ve deviation from ideal behaviour

Behaviour in some standard conditions

For 1 mole gas,

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

Also $\quad Z = \dfrac{PV_m}{RT}$

1. **For H_2 and He gas:**

   These are lightest gases present on earth (Mass of one particle ~ negligible)

   Type of IMAF $\Rightarrow$ London forces (Weakest)

   Also |IMAF| $\propto$ size ~ very very small

   i.e. $a \to 0$, put in equation (i)

   $(P + 0)(V_m - b) = RT$

   $PV_m - Pb = RT$

   $\boxed{Z = 1 + \dfrac{Pb}{RT}}$ i.e $Z > 1$ (always) $\Rightarrow$ repulsive forces dominantes.

2. **For typical real gases:** The behaviour of such gases varies with pressure.

   (i) At very low pressure ($P \to 0$)

i.e. very high $V_m \Rightarrow V_m^2$ very very high $\Rightarrow \left(\frac{1}{V_m^{\ 2}}\right)$ very very low

$$\left.\begin{array}{l}\left(P+\frac{a}{V_m^{\ 2}}\right)\sim P \\ (V_m - b)\sim V_m\end{array}\right\}\text{ Put in equation (i)}$$

$$(P)(V_m) \simeq RT$$

$\Rightarrow$ $\boxed{Z = 1}$ $\Rightarrow$ ideal behaviour

(ii) In low pressure range (P ~ 1 atm)

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

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

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

$$\because \left[(1-x)^{-1} = 1 + x + x^2 + ...\right] \quad \left[\because \left(\frac{b}{V_m}\right) < 1\ (\text{always})\right]$$

$$\text{So, } Z = \left[1 + \left(\frac{b}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + ...\right] - \frac{a}{V_m RT}$$

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

Low pressure $\Rightarrow$ High V_m

$\therefore$ $V_m^{\ 2}, V_m^{\ 3}, V_m^{\ 4}$..... very high

$\Rightarrow$ $\left(\frac{1}{V_m^{\ 2}}\right), \left(\frac{1}{V_m^{\ 3}}\right)$.... negligible

So, $\boxed{Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m}}$ in low pressure range.

Always $b < \frac{a}{RT}$

$\Rightarrow \boxed{Z < 1}$

If b is negligible then $Z = 1 - \frac{a}{V_m RT}$

(iii) In high pressure range

$$P >> \frac{a}{V_m^2} \Rightarrow \left(P + \frac{a}{V_m^2}\right) \sim P$$

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

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

e.g. H_2/He only

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

Other

Low pressure

$$\boxed{Z = 1 + \left(z - \frac{a}{RT}\right)\frac{1}{V_m}}$$

High pressure

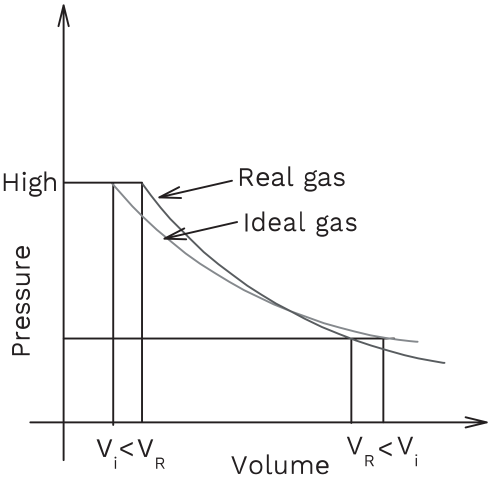
$$\boxed{Z = 1 + \frac{Pb}{RT}}$$

GRAPHS

1. **P vs V at constant temperature**

For ideal gas at constant temperature, PV = constant

For Typical Real Gas



In low P, $Z < 1$

$\Rightarrow$ $V_{real} < V_{ideal}$

In high P, $Z > 1$

$\Rightarrow$ $V_{Real} > V_{Ideal}$

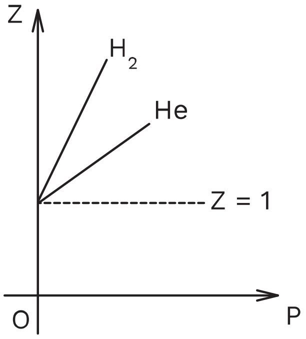
2. 'Z' vs 'P' graphs (at constant temperature)

Case-I:

For different gases at same temperature

(i) For H_2 and He gases

$$\boxed{Z} = 1 + \frac{b}{RT}P \qquad \text{...(1)}$$



Comparing equation (1) with line equations we get:

$$y = c + mx$$

$$\text{slope} = \left(\frac{b}{RT}\right)$$

Intercept = 1

$\because$ $(\text{Size})_{H_2} > (\text{Size})_{He}$

$\Rightarrow$ $(b)_{H_2} > (b)_{He}$

i.e. $(\text{Slope})_{H_2} > (\text{Slope})_{He}$

(ii) For typical real gas at very low pressure, Z = 1

(iii) At low pressure, $Z < 1$

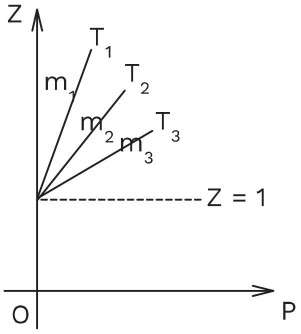
$$\left(Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m}\right)$$

Note: For typical real gas, if Z vs P graph is given, then to solve, use high pressure range.

For same gas at different temperature

At high pressure, $Z > 1$

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



(i) For H_2 or He gas

$$Z = \left(\frac{b}{RT}\right)P + 1$$

For a particular gas (b = constant)

$$m \propto \frac{1}{T}$$

i.e. if $T \uparrow \Rightarrow m \downarrow$

$\because \quad m_1 > m_2 > m_3$

$T_1 < T_2 < T_3$

(ii) For a typical real gas

In high pressure range

$$Z = \left(\frac{b}{RT}\right)P + 1$$

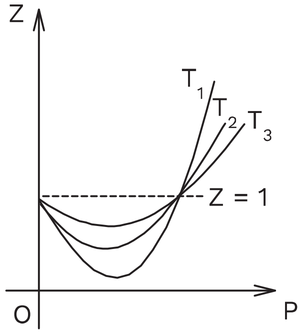
$$\text{Slope} = \left(\frac{b}{RT}\right)$$

For same gas (b = constant)

$$m \propto \frac{1}{T}$$

$\because \quad m_1 > m_2 > m_3$

$\Rightarrow \quad \boxed{T_1 < T_2 < T_3}$



Also, in low pressure range, as temperature increases, slope of curve also increases. So, at a certain temperature, the slope will become zero. This temperature is known as **Boyle's temperature**.

Boyle's Temperature & Liquefaction of gases

BOYLE'S TEMPERATURE

- The temperature at which a gas behaves ideally for considerable **low pressure range**.

  In low pressure,

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

  At $T = T_B \Rightarrow Z = 1$

  $$1 = 1 + \left(b - \frac{a}{RT_B}\right)\frac{1}{V_m}$$

  $$\Rightarrow \boxed{T_B = \frac{a}{R.b}}$$

ILLUSTRATION:

Q1 **A gas will deviate most from ideal behaviour at**

(A) low temperature and low pressure.

(B) low temperature and high pressure.

(C) low pressure and high temperature.

(D) high temperature and high pressure.

A1 B

At high pressure and low temperature, a gas deviates most from its ideal behaviour.

Q2 **For a real gas obeying Vander Waal's equation, a graph is plotted between PV_m (y-axis) and P(x-axis) where V_m is molar volume. Find y-intercept of the graph.**

A2 $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ for n moles, where 'a' and 'b' are Vander Waal's constants.

For

$n = 1$

$$PV_m = Pb - \frac{a}{V_m} + \frac{ab}{V_m^2} + RT$$

On comparing above equation with equation of straight line:

$$y = mx + c$$

y-intercept: $\frac{a}{V_m} - \frac{ab}{V_m^2} + RT$

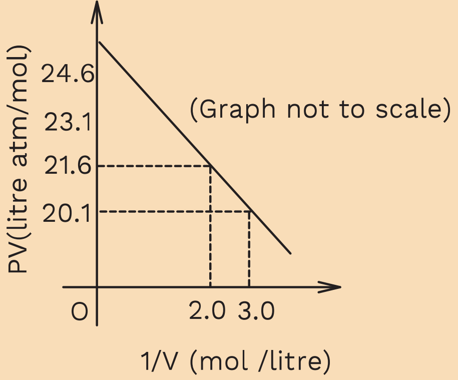
Q3 **For one mole of a vander Waal's gas when b= 0 and T = 300 K, the PV vs 1/V plot is shown below. The value of the vander Waal's constant a (atm. litre^2 mol^{-2}) is:**

(A) 1.0

(B) 4.5

(C) 1.5

(D) 3.0



A3 C

Vander Waal's equation:

$$\left(P + \frac{an^2}{V^2}\right)\left(V - nb\right) = nRT \qquad \text{...(i)}$$

Given b = 0 and n = 1 mole

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

$$PV_m + \frac{aV_m}{{V_m}^2} = RT$$

$$\left(PV_m\right) = RT - \frac{a}{\left(V_m\right)}$$

$$y = \left(-a\right)x + RT$$

$$\text{Slope} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$\left(-a\right) = \frac{20.1 - 21.6}{3 - 2}$$

$$-a = \frac{-1.5}{1}$$

$$\boxed{a = 1.5}$$

Q4 **One way of writing the equation for state for real gases is,**

$$\mathbf{P\bar{V} = RT\left[1 + \frac{B}{\bar{V}} + ...\right]}$$ **where B is a constant .**

Derive an approximate expression for 'B' in terms of vander Waal's constant 'a' and 'b'.

A4 Vander Waal's equation:

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

For 1 mole: $\left(P + \frac{a}{V^2}\right)\left(V - b\right) = RT$

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

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

$$PV = \frac{RTV}{(V - b)} - \frac{aV}{V^2}$$

$$PV = \frac{RTV}{V\left(1 - \frac{b}{V}\right)} - \frac{a}{V}$$

$$PV = \frac{RT}{\left(1 - \frac{b}{V}\right)} - \frac{a}{V}$$

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

$$PV = RT\left[1 + \frac{b}{V} + \frac{b^2}{V^2} + ...\right] - \frac{a}{V}$$

$$PV = RT\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + \frac{b^2}{V^2} + ...\right]$$

On comparing equation with

$$P\bar{V} = RT\left[1 + \frac{B}{V} + ...\right]; \boxed{B = \left(b - \frac{a}{RT}\right)}$$

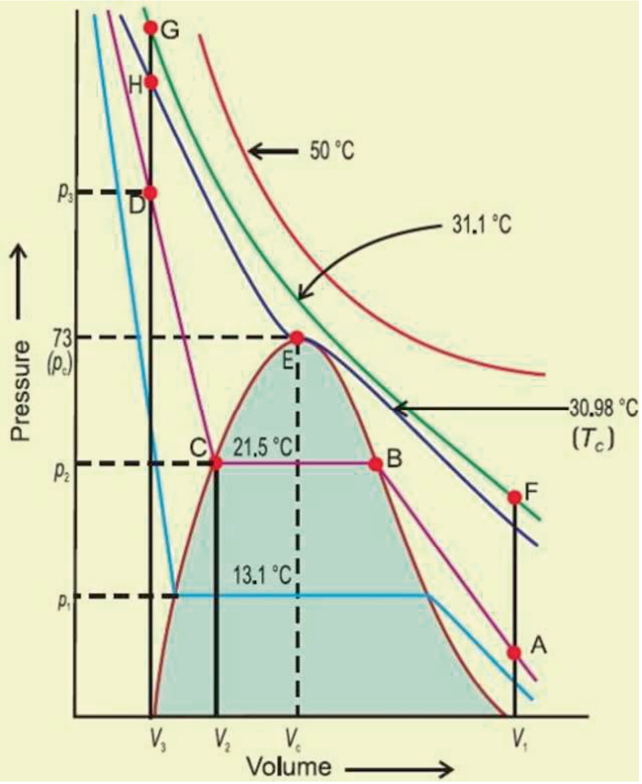
LIQUIFICATION OF GAS

- To liquify a gas, there must be attraction among particles hence an ideal gas can never be liquified.
- A gas can be liquified at constant temperature just by applying pressure on it.
- At a constant temperature, a certain minimum pressure is required for liquification.
- At higher temperature, the minimum required pressure for liquification will be higher, which can be explained by **Andrew's Isotherms.**

ANDREW'S ISOTHERMS

These are $\boxed{\text{P vs V}}$ graphs for a gas at different constant temperatures like T_1, T_2, T_3 and T_4 where $T_1 < T_2 < T_3 < T_4$

For 1 mole real gas



- At point A, gas is present at low pressure.

  From A to B,

  $P\uparrow \Rightarrow V\downarrow \;\Rightarrow$ Compression of gas
- At point B liquification starts means minimum required pressure for liquification at T =

21.5°C is P_2.

- From B to C gas liquifies at constant pressure P_2.
- After point C, no change in volume on pressure change means liquification is completed at C.
- At higher temperature, the minimum required pressure is higher than P_2 and also the horizontal segment becomes shorter due to more compression.
- At temperature T_C = 30.98°C, the gas liquifies at high pressure but liquid and gas phases cannot be distinguished at this pressure and temperature.
- Above temperature T_C, the gas cannot be liquified irrespective of any pressure hence T_C is known as **critical temperature**.

CRITICAL PRESSURE (P_c)

The minimum required pressure for liquification at T_C.

- The maximum temperature above which gas cannot be liquified at any pressure.
- Different gases have different values of their T_C.
- More value of T_C means more tendency to be liquified.

CRITICAL VOLUME (V_c)

The molar volume corresponding to T_C and P_C.

For gas

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

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

$$\boxed{V_c = 3b}$$

Note: $$\boxed{\frac{P_c V_c}{RT_c} = \frac{3}{8}}$$