

09/06/25

Gaseous state

There are two types of condition at which the gases is observed, on the basis of observation, it is classified into two types :-

(1) Ideal Gas

(2) Real gas

Ideal Gas

Real gas

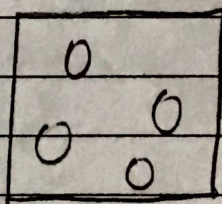
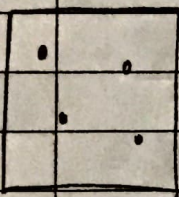
• Gaseous molecules are considered as point mass.

• Gaseous molecule are considered as dispersed mass.

[mass is distributed in a particular volume]

• There is no interactive force between gaseous molecule, either attractive or repulsive.

• There is interactive force between gaseous molecule, attractive as well as repulsive.



V_{ex} = volume excluded by gaseous molecule

V_{cont} = Volume of container

V_{av} = Available volume for free movement

$$V_{cont} = V_{ex} + V_{av}$$

For ideal gas

$$V_{ex} = 0$$

$$V_{cont} = V_{av}$$

For real gas

$$V_{ex} \neq 0$$

$$V_{cont} > V_{av}$$

• At very low pressure, volume of the container will become high. So, V_{ex} can be neglected in comparison of volume of

container. So, real gas can be considered as ideal gas under condition of low pressure.

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• At very high temperature, all the interactive forces between the molecules ~~are~~ get vanished, and real gas starts behaving like an ideal gas.

IMP

• At low pressure and high temperature, any real gas behave like an ideal gas.

Ideal Gas

Gaseous Parameter -

All the variable by which a gaseous state is identified is known as gaseous parameter.

$$\begin{aligned} P &= P_1 \\ V &= V_1 \\ T &= T_1 \end{aligned}$$

System - 1

Pressure, volume and temperature are fundamental gaseous parameter or variable.

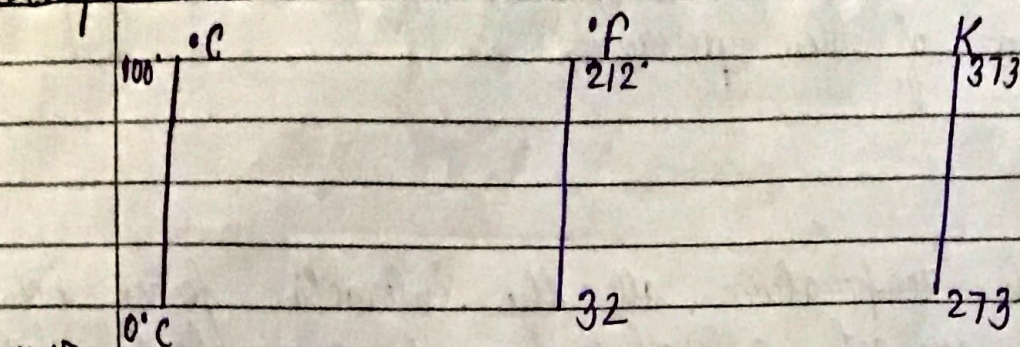
~~Non~~ • There are non-fundamental variable, i.e., internal energy (U), enthalpy (H), entropy (S), Gibbs free energy (G).

(1) Volume -

• Used in litre

$$\left[\begin{aligned} V &= 1 \text{ m}^3 = 1000 \text{ lit} \\ 1 \text{ dm}^3 &= 1 \text{ L} \\ 1 \text{ L} &= 1000 \text{ mL} \\ 1 \text{ mL} &= 1 \text{ cm}^3 \end{aligned} \right]$$

(2) Temperature -



$$\frac{C-0}{100-0} = \frac{F-32}{212-32} = \frac{K-273}{373-273}$$

Q1) Convert 25°C into $^{\circ}\text{F}$.

$$\frac{C}{5} = \frac{F-32}{9}$$

$$\Rightarrow 5 \times 9 = F - 32$$

$$\Rightarrow 45 + 32 = F = \boxed{77^{\circ}\text{F}}$$

Q2) At what temperature the $^{\circ}\text{F}$

Q2) Convert 300K into Fahrenheit.

$$^{\circ}\text{C} = 300 - 273$$

$$= 27^{\circ}$$

$$\frac{27}{5} = \frac{F-32}{9}$$

$$\Rightarrow \frac{243}{5} + 32 = F$$

$$\Rightarrow 48.6 + 32 = F$$

$$\Rightarrow \boxed{80.6^{\circ}\text{F}}$$

(3) Pressure -

Force exerted by the gaseous molecule on the wall of the container per unit area is known as pressure.

$$\begin{aligned}
 P &= 1 \text{ atm} \\
 1 \text{ atm} &= 1.03 \times 10^5 \text{ Pa (N/m}^2\text{)} \\
 1 \text{ atm} &= 760 \text{ mm of Hg} \\
 1 \text{ atm} &= 760 \text{ torr} \\
 1 \text{ atm} &= 1.01 \text{ bar} \\
 1 \text{ atm} &= 76 \text{ cm of Hg}
 \end{aligned}$$

Pressure measuring device:

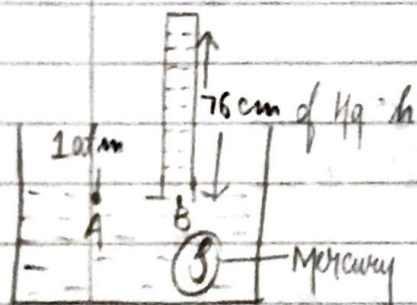
Barometer

Manometer

close end
manometer

open end
manometer

Barometer-



Pressure at point A = pressure at point B
[same height]

$$\begin{aligned}
 P_{\text{atm}} &= P_{\text{Hg column}} \\
 &= \frac{F}{A}
 \end{aligned}$$

$$= \frac{mg}{A} = \frac{V \cdot S \cdot g}{A}$$

$$= \frac{A \cdot h \cdot S \cdot g}{A}$$

$$P_{\text{atm}} = Sgh$$

When mercury liquid is taken, and it is kept in 1 atm pressure,

$$P = 1 \text{ atm}; S = 13.7 \text{ g/mL}$$

$$P = Sgh$$

$$\Rightarrow 10^5 \text{ Pa}$$

$$h = 76 \text{ cm}$$

When a given pressure is measured for two different liquid having density S_1 and S_2 , then

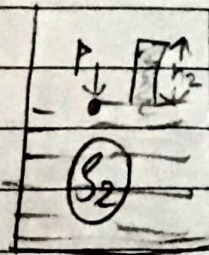
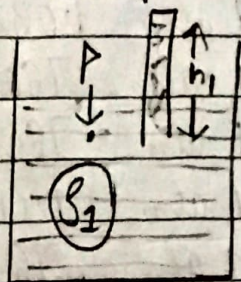
$$P_1 = h_1 \rho_1 g$$

Given, $P_1 = P_2$

$$P_2 = h_2 \rho_2 g$$

$$h_1 \rho_1 g = h_2 \rho_2 g$$

$$\Rightarrow h_1 \rho_1 = h_2 \rho_2$$



Q1 Find the atmospheric pressure (in atm) when a liquid having density 6.8 g/cm^3 rises to a height of 76 cm in barometric analysis.

$$\rho = 6.8 \text{ g/ml}$$

$$= 6800 \text{ kg/m}^3$$

$$h = 76 \text{ cm}$$

$$= 0.76 \text{ m}$$

$$P = 6800 \times 0.76 \times 10$$

$$= 2 \times 10^5 \text{ Pa}$$

$$h_1 \rho_1 = h_2 \rho_2$$

$$\Rightarrow 76 \times 6.8 = h \times 13.6$$

$$\Rightarrow h = \frac{76}{2} = 38 \text{ cm}$$

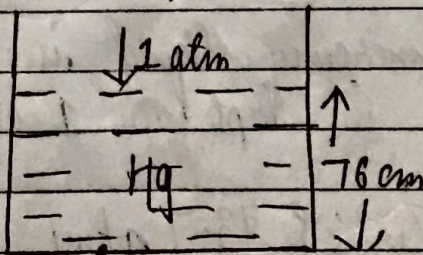
$$\therefore \text{Pressure} = 2 \text{ atm}$$

$$\text{For Hg, } 76 \text{ cm} = 1 \text{ atm}$$

$$38 \text{ cm} = 0.5 \text{ atm}$$

Q2 Find the pressure at the bottom of the container.

$$1 + 1 = 2 \text{ atm}$$

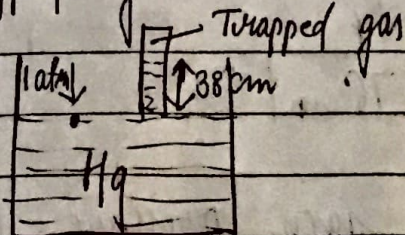


Q3 Find the pressure of the trapped gas in a barometer (in atm)?

Trapped gas =

$$1 \text{ atm} - 0.5 \text{ atm}$$

$$= 0.5 \text{ atm}$$

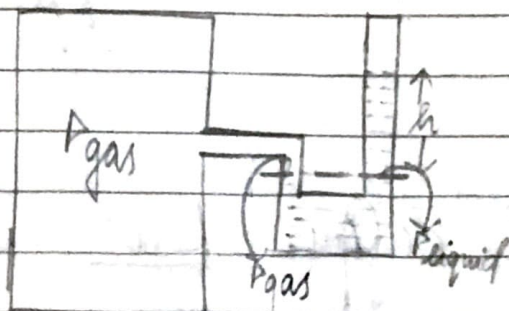


- If some gas is present inside barometer (not totally vacuum), it is called faulty barometer.

Manometer -

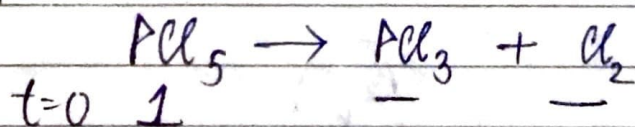
$$P_{\text{gas}} = P_{\text{liquid}}$$

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



Closed-end manometer

- Q1) 1 mole of PCl_5 is taken in closed-end manometer tube having initial height of the liquid column 20 cm of Hg. After heating the sample, the gaseous molecule dissociate into PCl_3 and Cl_2 . The degree of dissociation of the reaction is 0.4. Find the % change in height of liquid column.



$$t=0 \quad 1$$

$$t=t \quad 0.6$$

$$0.4$$

$$0.4$$

$$\text{Total moles} = 0.6 + 0.4 + 0.4$$

$$= 1.4n$$

$$1n = 20 \text{ cm}$$

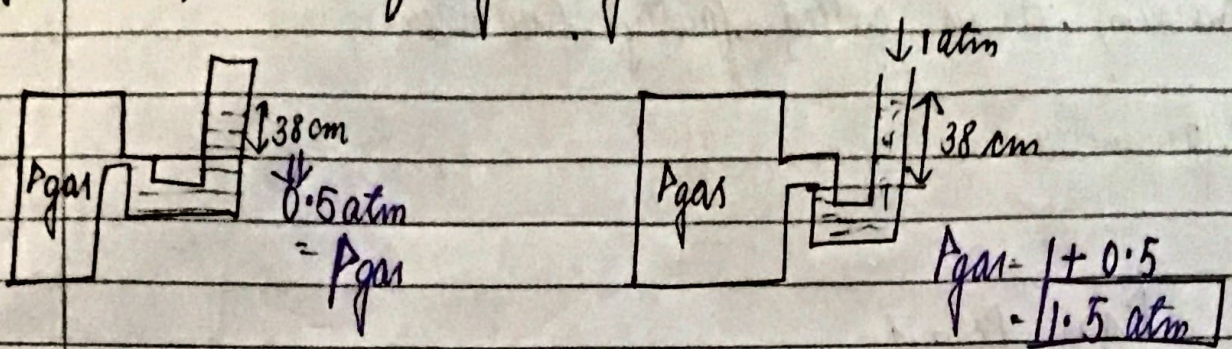
$$1.4n = 20 \times 1.4$$

$$= 28 \text{ cm}$$

$$\% \text{ change} = \frac{8}{20} \times 100 = 40\%$$

Q2)

Q2 Find the pressure of gas given in manometer



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(1) Boyle's Law

At constant temperature and for a fixed amount of gas, pressure of gas is inversely proportional to its volume.

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

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

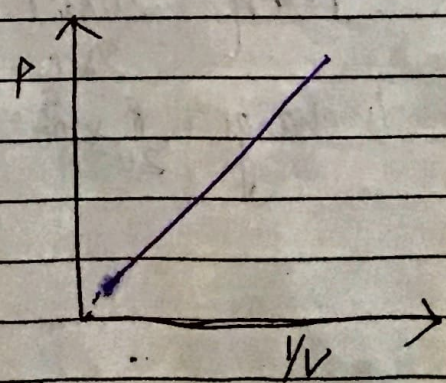
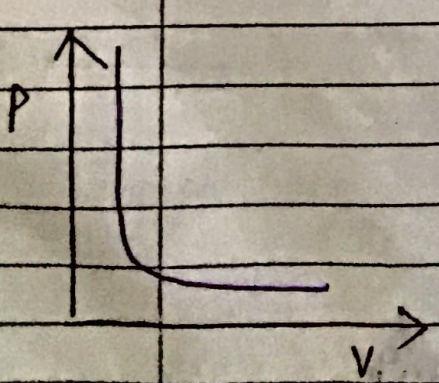
$$PV = k$$

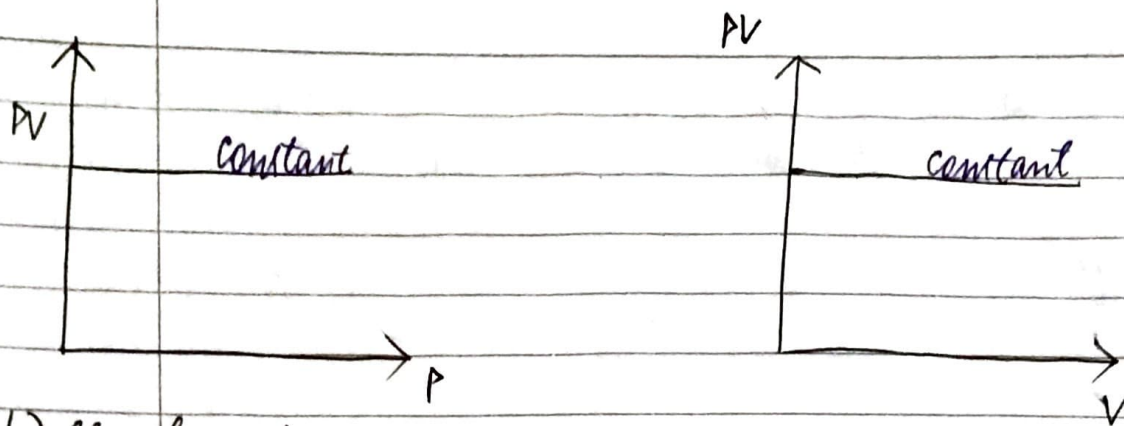
$$\left(\frac{P_1}{V_1} \right)_{T, n}$$

$$\left(\frac{P_2}{V_2} \right)_{T, n} \text{ System 2}$$

System 1

$$P_1 V_1 = P_2 V_2 = \dots = P_n V_n$$





(2) Charles Law -

For a fixed amount of gas, volume of the gaseous system is directly proportional to its temperature (absolute temperature).

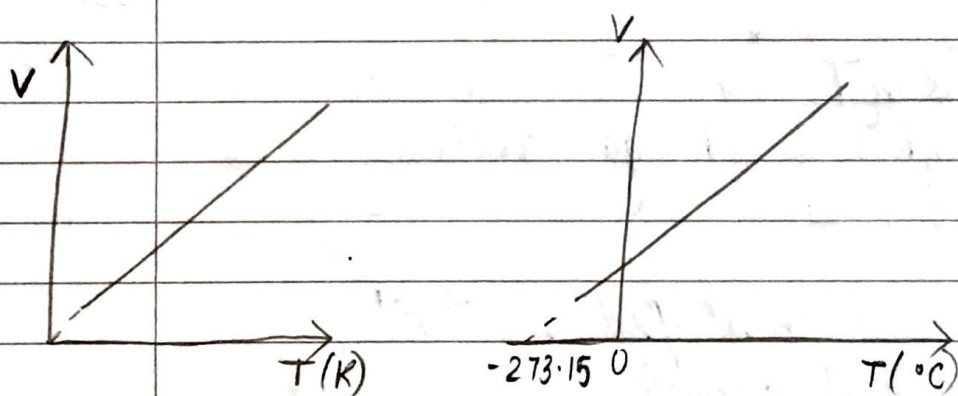
$$P, n \rightarrow \text{constant}$$

$$V \propto T$$

$$V = kT$$

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

When temperature is measured in Kelvin, it is called absolute temperature.

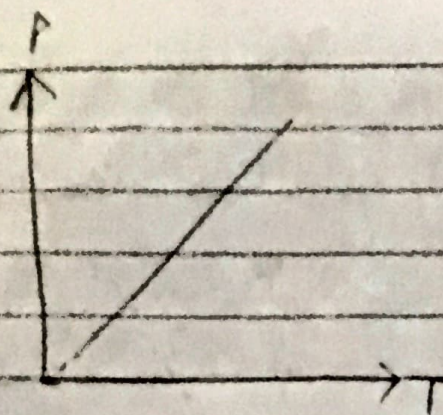


(3) Gay Lussac Law -

For a fixed amount of gas, pressure of any gaseous system is directly proportional to absolute temperature, at constant volume.

$$P \propto T$$

$$P = kT \Rightarrow \boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2} = k} = \text{MAYBE}$$



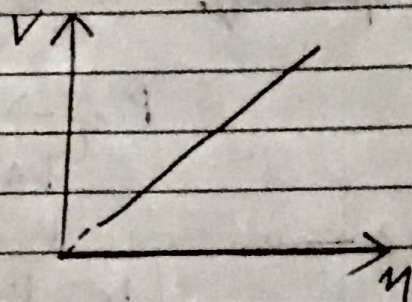
(4) Avogadro's Law -

At constant pressure and temperature, volume of the gas is directly proportional to its no. of moles.

$$V \propto n$$

$$V = kn$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \dots = k$$



After combining all gas laws.

$$\frac{PV \propto nT}{PV = nRT} \quad [R = \text{gas constant}]$$

$$\left[\begin{aligned} R &= 0.0821 \text{ atm/lit mol}^{-1} \text{ K}^{-1} \\ &= 8.31 \text{ J/mole} \\ &= 2 \text{ cal/mole} \end{aligned} \right]$$

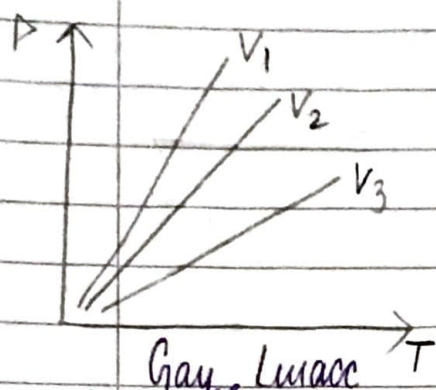
$$PV = nRT$$

$$\Rightarrow PV = \frac{\text{given mass (W)}}{\text{molar mass (M)}} RT$$

$$\Rightarrow PM = \frac{W}{V} RT$$

$$\Rightarrow \boxed{PM = dRT} \quad [d \text{ in g/lit}]$$

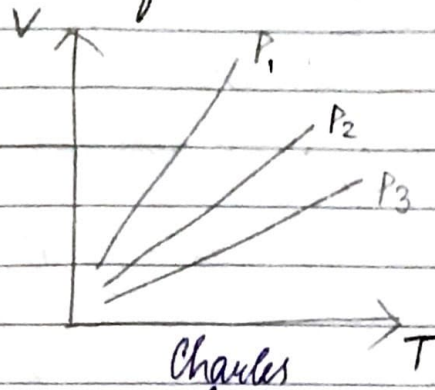
Q1 ~~Some~~ 3 different graphs have been plotted at 3 different volumes, V_1, V_2 & V_3 . Write the order of V_1, V_2 & V_3 .



Gay Lussac
 $P = \left(\frac{nR}{V} \right) T$ (slope)

$$\frac{nR}{V_1} > \frac{nR}{V_2} > \frac{nR}{V_3}$$

$$\Rightarrow V_1 < V_2 < V_3$$



Charles
 $V = \left(\frac{nR}{P} \right) T$

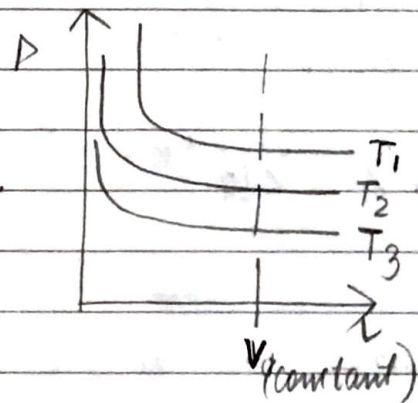
$$\frac{nR}{P_1} > \frac{nR}{P_2} > \frac{nR}{P_3}$$

$$\Rightarrow P_1 < P_2 < P_3$$

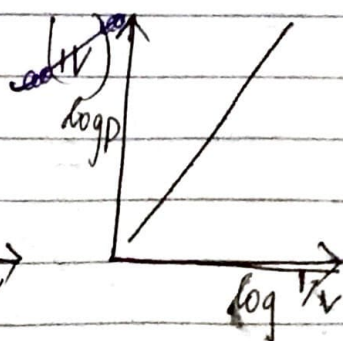
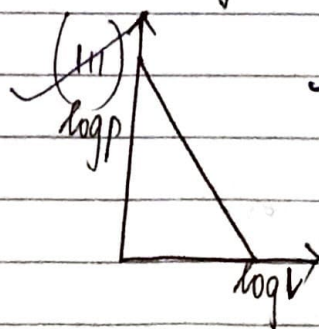
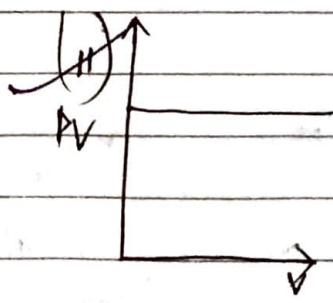
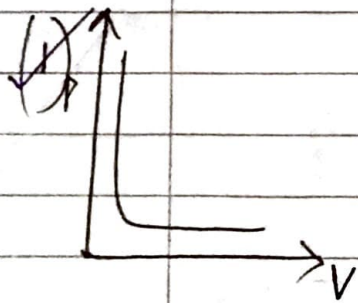
Q2 Order of $T_1, T_2, T_3 = ?$

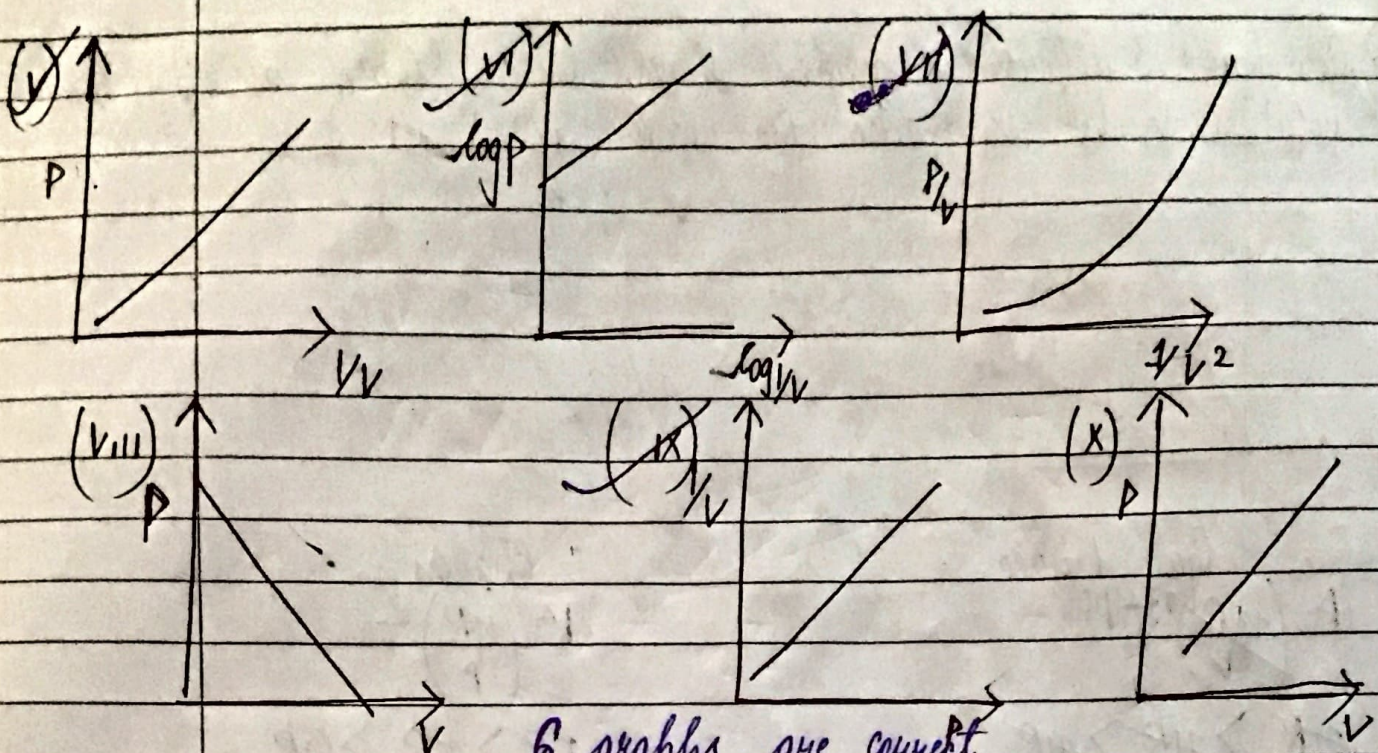
Pressure for T_1 is max.
 at constant volume V_0 .

$$T_1 > T_2 > T_3$$



Q3 How many of the following explain Boyle's Law?





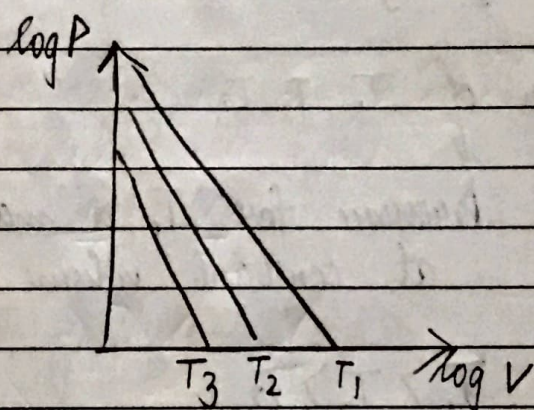
6 graphs are correct

(Q4) Compare T_1, T_2 & T_3 .

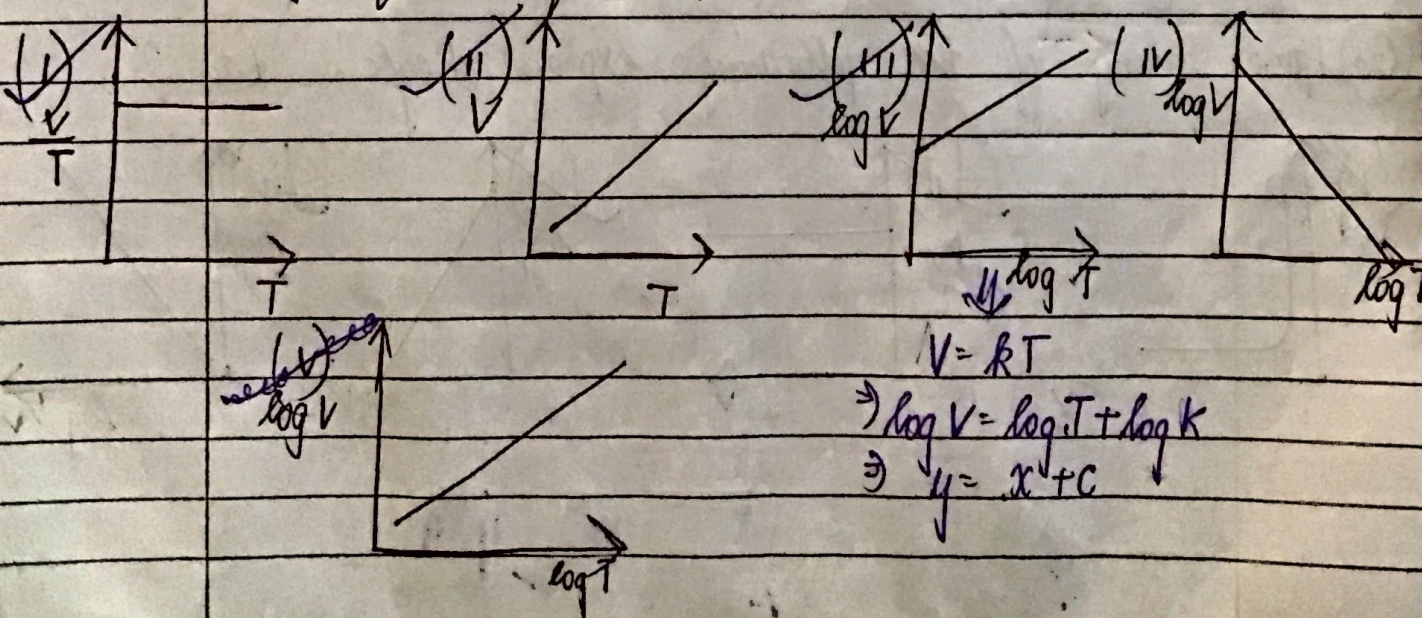
$$PV = nRT$$

$$\log P + \log V = nRT$$

$$T_1 > T_2 > T_3$$



(Q5) How many of the following are correct for Charles' law?



$$V = kT$$

$$\Rightarrow \log V = \log T + \log k$$

$$\Rightarrow y = x + c$$

(Q6) Pressure of any gaseous system is 1 atm having volume 2 litre. The volume of the system is expanded till 10 lit isothermally (constant temperature). Find the % change in pressure.

$$P_1 V_1 = P_2 V_2$$

$$\Rightarrow 1 \times 2 = P \times 10$$

$$\Rightarrow P = \frac{1}{5} \text{ atm}$$

$$\therefore \% \text{ change} = \frac{4}{5} \times 100 = 80\% \text{ decrease}$$

(Q7) A gaseous mixture of $\overset{\uparrow}{\text{CO}}$ and $\overset{\uparrow}{\text{CO}_2}$ is found to have density 1.5 g/lit at 30°C and 730 mm of Hg pressure. Find the molar composition of gases in the mixture.
 $\begin{array}{c} 760 \text{ mm of Hg} \\ | \quad | \\ 1 \quad 1 \\ \hline 2 \end{array} \rightarrow 1 \text{ atm}$

$$730 \text{ mm} = \frac{1}{760} \times 730 = \frac{73}{76} \text{ atm}$$

$$\left(\frac{73}{76} \right) (M) = \frac{15}{102} \times 0.0821 \times 303$$

$$\Rightarrow M = \frac{3 \times 0.0821 \times 303 \times 38}{73}$$

$$\frac{3 \times 1}{12} \times 303 \times 38 = \frac{44x + 28y}{x+y}$$

$$\Rightarrow \frac{2727}{73} = \frac{44x + 28y}{x+y}$$

$$\Rightarrow 2727x + 2727y = 3212x + 2044y$$

$$\Rightarrow 2727y - 2044y = 3212x - 2727x$$

$$\Rightarrow 683y = 485x$$

$$\Rightarrow \frac{x}{y} = \frac{683}{485}$$

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Q1) An open container contains air heated from 200K to 400K. Find the % of gas escaped from the container.

$P = 1 \text{ atm}$

Initial volume = V Volume is constant as container is open.
Volume is same.

$$V = n_1 R 200$$

Final =

$$V = n_2 R 400$$

$$\therefore \% \text{ change} = \frac{200 - 100}{100} \times 100 = 100\%$$

$$n_1 T_1 = n_2 T_2$$

$$\Rightarrow n_1 200 = n_2 400$$

$$\Rightarrow \frac{n_1}{n_2} = 2$$

$\therefore 50\%$ gas is escaped

Q2) A balloon is filled to $\frac{7}{8}$ th of its max. volume at 27°C . At what temperature the balloon will burst?

$$\frac{7}{8} V \times 300 = V \cdot T \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \frac{7 \times 75}{2} = T \quad \Rightarrow \frac{7/8 V}{300} = \frac{V}{T}$$

$$\Rightarrow T = 525 = 262.5^\circ\text{C} \quad \Rightarrow T = \frac{300 \times 8}{7} = 342.8^\circ\text{C}$$

$$T > 342.4^\circ\text{C}$$

Q3) An underwater bubble with radius 0.5 cm at the bottom of the tank where temp. is 5°C & pressure 3 atm rises to the surface of liquid at the temperature of 27°C . Find the % change of radius of bubble?

$$\text{Volume of bubble} = \frac{4}{3} \pi r^3$$

or

Initial temperature = 278K
 $\frac{3 \times 4\pi r_1^3}{3} = \eta R 278$

Final,
 $\frac{1 \times 4\pi r_2^3}{3} = \eta R 300$

$\Rightarrow \frac{4\pi r_1^3}{3} = \eta R 278$
 $\frac{4\pi r_2^3}{3} = \eta R 300$

$\Rightarrow \frac{4\pi r_1^3}{3} \times \frac{3}{4\pi r_2^3} = \frac{\eta R 278}{\eta R 300} = \frac{278}{300}$

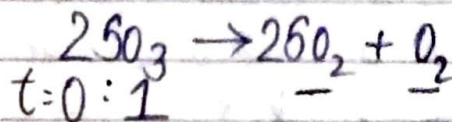
$\Rightarrow \frac{r_1^3}{r_2^3} = \frac{278}{300}$

$\Rightarrow \frac{300 \times 3 \times 0.5 \times 0.5 \times 0.5}{278} = r_2^3 = \frac{50}{124}$

$= 0.75 \text{ cm}$

$\therefore \% \text{ change} = \frac{0.25}{0.5} \times 100 = 50\%$

Q4 A closed container contain SO_3 gas at 300K . The container was heated till 600K . The SO_3 dissociate into SO_2 & O_2 , having degree of dissociation 0.5. Find the % change in pressure.



$t=0: 1$

$t=\infty: 1-x \quad 2x \quad x/2$

$t=\infty: 0.5 \quad 0.5 \quad 0.25$

Initially, $PV = \eta R 300$

$\Rightarrow P = R 300$

$\Rightarrow V = \frac{R 300}{P_1}$

Final, $P_2 V = 1.25 R 600$

$\Rightarrow P_2 \frac{R 300}{P_1} = 800 \times 1.25 R$

$\Rightarrow \frac{P_2}{P_1} = 2.50$

$$\% \text{ change} = \frac{1.5 \times 100}{150} = 1\%$$

(Q5) An open container at 27°C is heated until $\frac{3}{5}$ th part of the air has been escaped. Find the temp. at which it was heated.

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

$$\Rightarrow \frac{V}{300} = \frac{\frac{2}{5}V}{T}$$

$$\Rightarrow T = 120$$

V is same as container is open

$$P_1 V_1 = n_1 R T_1$$

$$P_2 V_2 = n_2 R T_2$$

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

$$\Rightarrow \frac{V}{300} = \frac{\frac{2}{5}V}{T}$$

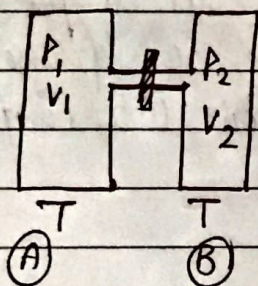
$$\Rightarrow T = 120$$

$$\Rightarrow \boxed{750\text{K} = T}$$

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Problem Related With Connecting Valve:-

Case - 1: Identical temperature



$$\eta_A = \frac{P_1 V_1}{RT}$$

$$\eta_B = \frac{P_2 V_2}{RT}$$

After removal of the stopcock the whole system will behave like a single container.

$$V_f = V_1 + V_2$$

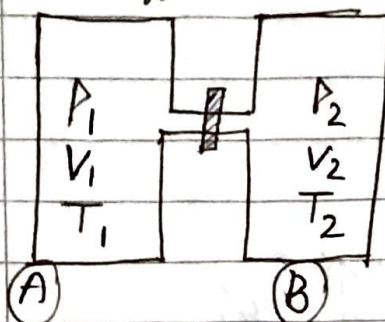
$$P_f = ?$$

$$(\eta_A + \eta_B) = (\eta_f)$$

$$\frac{P_1 V_1}{RT} + \frac{P_2 V_2}{RT} = \frac{P_f (V_1 + V_2)}{RT}$$

$$\Rightarrow \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2} = P_f$$

Case-2 : Different temperature



• T_1 and T_2 temperature has been maintained for the valve.

• Volume of connecting pipe is considered to be negligible.

$$n_A = \frac{P_1 V_1}{RT_1} ; n_B = \frac{P_2 V_2}{RT_2}$$

After removal of stopcock,

$$(n_A + n_B)_i = (n_A + n_B)_f$$

$$\Rightarrow \frac{P_1 V_1}{RT_1} + \frac{P_2 V_2}{RT_2} = \frac{P_f V_1}{RT_1} + \frac{P_f V_2}{RT_2}$$

$$\Rightarrow \boxed{\frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2} = \frac{P_f V_1}{T_1} + \frac{P_f V_2}{T_2}}$$

Dalton's Law of Partial Pressure :-

According to the law, the total pressure exerted by a gaseous mixture is sum of the individual pressure of the gases in a particular container.

$$P_A = \frac{n_A RT}{V}$$

$$P_B = \frac{n_B RT}{V}$$

$$P_C = \frac{n_C RT}{V}$$

$$P_T = \frac{(n_A + n_B + n_C) RT}{V}$$

$$\begin{array}{l} A \rightarrow n_A \\ B \rightarrow n_B \\ C \rightarrow n_C \end{array}$$

V, T

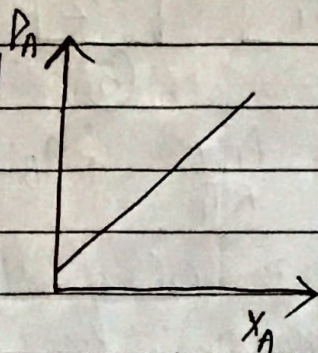
$$\Rightarrow P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} \Rightarrow \boxed{P_T = P_A + P_B + P_C}$$

On dividing P_A/P_T ,

$$\frac{P_A}{P_T} = \frac{n_A RT}{(n_A + n_B + n_C) RT} = \frac{n_A}{n_A + n_B + n_C}$$

$$\Rightarrow \frac{P_A}{P_T} = X_A \text{ [Mole fraction]}$$

$$\Rightarrow \boxed{P_A = P_T X_A}$$



Some Important Points:-

- (1) Pressure applied by individual gas in a gaseous mixture is known as partial pressure.
- (2) Partial pressure of the gas is directly proportional to its mole fraction.

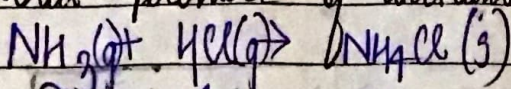
(Q1) A closed container contain gaseous mixture at a total pressure of 15 atm, of Helium and Oxygen gas. The mole fraction of He is 0.2. Find the partial pressure of O_2 .

$$P_T = 15$$

$$X_O = 1 - 0.2 = 0.8$$

$$\text{Partial pressure of } O_2 = 15 \times 0.8 = 12 \text{ atm.}$$

(Q2) 2 mole of ammonia gas (NH_3) & 1 mole of HCl gas are taken in a container of volume 8.2 L, at a temperature of 300 K. Find total pressure of container.



$$t=0 \quad 2 \quad 1 \quad -$$

//_

$t = \infty$ 1 - 1 [No pressure] (solid doesn't apply pressure)
 Total moles in container = 21
 $P(8.21) = 12 \times 0.0821 \times 300$
 $\Rightarrow P = \frac{3000 \times 821}{82100} = 3 \text{ atm}$

- (3) Pressure applied by any solid substance is considered to be negligible (not zero), as compared to gaseous substance.
- (4) Gases present in container should be non-reacting.
- (5) Pressure applied by the liquid is known as vapour pressure of the liquid.

Vapour Pressure of Liquid-

- Pressure applied by the gaseous molecule of the liquid over the surface of the liquid is known as vapour pressure.

Characteristics of Vapour Pressure:

- Vapour pressure is temperature dependent only.
- Boyle's law is not applicable to vapour pressure of liquid.

$$P = \frac{nR}{V} T$$

$\text{lid} \uparrow \quad \text{vol} \uparrow \quad n \uparrow$ (for nR to be constant)
 $\downarrow$
 liquid is evaporating

Q1) Gaseous N_2 is collected over liquid water at atmospheric pressure of 1 atm. The volume of the gaseous substance is doubled at a constant temp. Find the final pressure over the liquid (atm). The aqueous tension of water is 0.1 atm.

Final pressure after doubling volume =	$\frac{0.9}{2} + 0.1 = \frac{0.45 + 0.1}{1} = 0.55 \text{ atm}$
--	---

$$\begin{array}{c} 0.9 \quad 0.1 \\ \text{N}_2 + \text{H}_2\text{O} \end{array}$$

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Q2) 96 g of ozone gas converts into oxygen at a pressure of 1 atm and 600K temperature. The ~~part~~ of the ~~mass~~ ozone is 0.4. Find the partial pressure of oxygen & ozone in the container.

$$2O_3 \rightarrow 3O_2$$

t=0	2n	—
t=t	2-0.8	1.2
	= 1.2n	0.8n

∴ Mole fraction of oxygen = $\frac{1.2}{2.0} = \frac{3}{5}$ 1.2 : 0.8 = 3 : 2

Partial pressure of oxygen = 0.6 atm

Partial pressure of ozone = 0.4 atm

Relative Humidity—

Humidity: When dry air absorbs some gaseous water molecule then this is known as humid air. The phenomena is known as humidity.

//_

At a fixed temperature, a particular amount of dry air have a fixed capacity to absorb moisture. When the air contain max. capacity of moisture, then this is known as 100% humid air, or if the air contain lesser amount then maximum capacity of moisture then this is known as partially humid air.

$$\% \text{ humidity} = \frac{\text{pressure of } H_2O}{\text{Max. partial pressure of } H_2O (V.P.)} \times 100$$

Q1) What is the density of moist air having relative humidity 75% at a total pressure of 1 atm & temperature 300K? [Vapour pressure of H_2O is 30 mm of Hg at temperature of 300 K] [Avg. molar mass of air = 29]

~~$$75 = \frac{30}{P_{H_2O}} \times 100$$~~

~~$$\Rightarrow P_{H_2O} = 40$$~~

~~$$40 \times 29 = \frac{1}{12} \times 300$$~~

~~$$\Rightarrow \frac{8 \times 29}{5} = \frac{232}{5} = 46.4 \text{ g/lit}$$~~

$$M_{\text{avg.}} = \frac{29 \times \frac{747.5}{760} + 18 \times \frac{22.5}{760}}{1}$$

1

$$\therefore PM = dRT$$

$$\Rightarrow 1 \times \left(29 \times \frac{747.5}{760} + 18 \times \frac{22.5}{760} \right) = d \times \frac{1}{12} \times 300$$

$\Rightarrow$

$$75 = \frac{P_{H_2O} (\text{present in dry air})}{30} \times 100$$

$$\Rightarrow P_{H_2O} = \frac{75 \times 30}{100} = 22.5$$

$$\begin{aligned} \text{Total pressure} &= 760 \text{ mm of Hg} \\ \text{pressure due to dry air} &= 760 - 22.5 \\ &= 747.5 \text{ mm of Hg} \end{aligned}$$

Q Humid air have total pressure 1 atm having relative humidity 50%. The vapour pressure of water is 50 mm of Hg at that temperature. Find the mole fraction of water molecule in humid air.

$$\frac{25}{50} = \frac{P_{H_2O} \text{ (present in dry air)}}{50} \times 100$$

$\Rightarrow$ 25 mm of Hg of H_2O present in 760 mm of Hg of moist air.

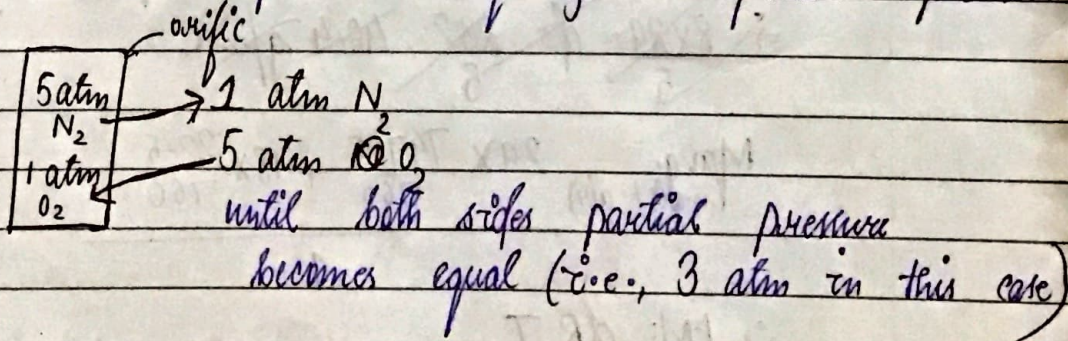
$$\therefore \text{Mole fraction} = \frac{25}{760} = \frac{5}{152}$$

Diffusion and Effusion :-

Diffusion - Spontaneous mixing of two different gases is known as diffusion.

Effusion - Accelerated diffusion or diffusion taking place from a small orifice (hole/opening) is known as effusion.

Diffusion process take place to equalize the partial pressure.



Graham's Law of Diffusion -

The initial rate of diffusion is directly proportional to the partial pressure of the gas.

$$\alpha \propto P$$

$$\alpha \propto \frac{1}{\sqrt{M_{\text{gas}}}}$$

$$[M_{\text{gas}} = \text{Molar mass of gas}]$$

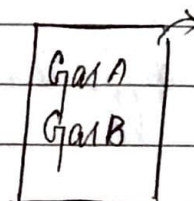
$$\alpha = \frac{KP}{\sqrt{M}}$$

$$K = \frac{A_0 N_A T}{\sqrt{2\pi R}}$$

$$\left[\begin{array}{l} A_0 = \text{area of the orifice} \\ N_A = \text{Avogadro's number} \\ T = \text{temperature} \\ R = \text{gas constant} \end{array} \right]$$

If the gases are diffusing/effusing from same orifice at same temperature,

$$\frac{v_A}{v_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}}$$



Some Important Points -

(1) When two different gas, effusing from same container,

$$P \propto n$$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$\frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$

(2) The rate of effusion can be considered constant for a time being. It can be given

$$r = \frac{\Delta P}{\Delta t} \quad \left(\begin{array}{l} \text{decrease in} \\ \text{pressure} \end{array} \right)$$

[atm/s]

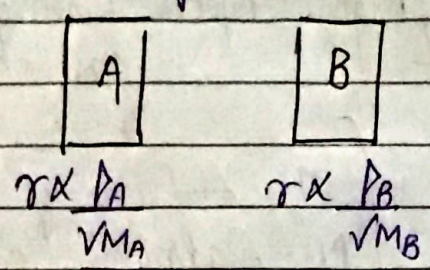
$$r = \frac{\Delta n}{\Delta t} \quad \left(\begin{array}{l} \text{decrease in} \\ \text{no. of moles} \end{array} \right)$$

[mol/s]

$$r = \frac{\Delta V}{\Delta t} \quad \left(\begin{array}{l} \text{decrease in} \\ \text{volume} \end{array} \right)$$

[mL/s]

(3) When two different gases are effusing from different containers having identical orifice -

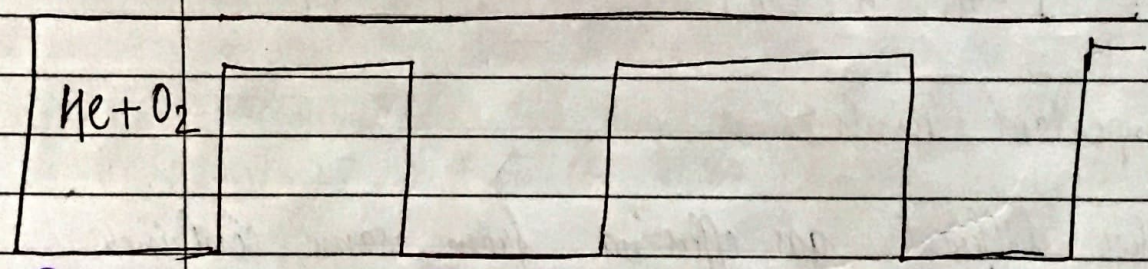


$$\frac{r_A}{r_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \quad \text{can't be replaced by } \frac{n_A}{n_B}$$

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Enrichment of Gas:-

Continuous diffusion process is applied for the enrichment process.



50% He
50% O₂

70% He
30% O₂

85% He
15% O₂

$$\frac{r_{He}}{r_{O_2}} = \frac{n_{He}}{n_{O_2}} \sqrt{\frac{M_{O_2}}{M_{He}}} \quad \text{(for 1st effusion)}$$

For 2nd effusion,
 $\frac{n'_{He}}{n'_{O_2}} = \text{ratio of rate of 1st effusion}$

$$\left(\frac{r_{He}}{r_{O_2}} \right)_2 = \frac{n_{He}}{n_{O_2}} \sqrt{\frac{M_{O_2}}{M_{He}}}$$

$$\Rightarrow \frac{(M_{He})_2}{(M_{O_2})_2} = \left(\frac{n_{He}}{n_{O_2}} \right) \left(\sqrt{\frac{M_{O_2}}{M_{He}}} \right) \left(\sqrt{\frac{M_{O_2}}{M_{He}}} \right)$$

For 2nd container,

$$\left(\frac{n_{He}}{n_{O_2}} \right)_{II} = \frac{n_{He}''}{n_{O_2}''} \sqrt{\frac{M_{O_2}}{M_{He}}}$$

$\frac{n_{He}''}{n_{O_2}''}$ = ratio of mole of effusion of 2nd container

$$\frac{n_{He}''}{n_{O_2}''} = \frac{n_{He}}{n_{O_2}} \left(\frac{M_{O_2}}{M_{He}} \right)^{3/2}$$

$$\therefore \left(\frac{n_{He}}{n_{O_2}} \right)_{II} = \frac{n_{He}}{n_{O_2}} \left(\frac{M_{O_2}}{M_{He}} \right)^{3/2}$$

For n^{th} container,

$$\frac{M_X}{M_Y} = \frac{n_X}{n_Y} \left(\frac{M_Y}{M_X} \right)^{n/2}$$

• The method is used to separate mixture of gaseous substance having considerable difference in molar mass.

• It is used to separate H_2 and D_2 gas.

• Higher the ratio of ~~in~~ molar mass, greater will be the ease of separation.

• Higher the ratio of molar mass, lesser effusion step will be required to separate the mixture of gas.

Kinetic Theory of Gases (KTG) -

Some Postulates of KTG:

- Gaseous molecules are considered as point mass.
- All the collision taking place between the gaseous molecule are elastic in nature (energy remains conserved).
- All the interactions between the molecule, either attractive or repulsive, are negligible.
- Molecules travel in straight line before each collision. This type of motion is known as Brownian motion & due to ~~Brownian~~ motion, it remain in dispersed form.
- Kinetic energy of any molecule is directly proportional to temperature.

$$KE \propto T \text{ (in Kelvin)}$$

$$\frac{1}{2} mv^2 = \frac{3}{2} PV \text{ (By derivation)}$$

$$KE = \frac{3}{2} RT \text{ (for 1 mole)}$$

$$\text{total } KE = \frac{3}{2} nRT \text{ (for } n \text{ mole)}$$

$$KE \text{ (per molecule)} = \frac{3}{2} \frac{RT}{N_A}$$

$$\Rightarrow \frac{3}{2} \left(\frac{R}{N_A} \right) T$$

$$\Rightarrow \boxed{\frac{3}{2} KT}$$

$$\left[\begin{array}{l} K = \text{Boltzman const.} \\ = 1.3 \times 10^{-23} \text{ J/Kelvin} \end{array} \right]$$

Q1 Find the KE for 1 mole of He gas at 27°C.

$$KE = \frac{3}{2} \times 8.31 \times 300$$

$$\Rightarrow KE = 450 \times 8.31$$

$$= \boxed{3739.5 \text{ J}}$$

- Kinetic energy of the gaseous molecule is temperature dependent only.
- The value of R will be taken as 8.31 J/mole/Kelvin.
- On the basis of KE, 3 type of molecular speed is given:

(i) V_{mps} (~~Max~~ Most Probable Speed)

(ii) V_{avg} (Average speed)

(iii) V_{rms} (Root Mean Square Speed)

e.g.

70 mol - 100 m/s
10 mol - 400 m/s
20 mol - 50 m/s
100 molecule

$$V_{mps} = 100 \text{ m/s [Max. molecule]}$$

$$V_{avg} = \frac{70 \times 100 + 10 \times 400 + 20 \times 50}{100}$$

$$V_{rms} = \sqrt{\frac{70(100)^2 + 10(400)^2 + 20(50)^2}{100}}$$

$$V_{rms} = \sqrt{\frac{3RT}{M}}$$

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

$$V_{mps} = \sqrt{\frac{2RT}{M}}$$

M = Molar Mass (in kg)
 T = Temperature (in Kelvin)
 R = Gaseous constant
 (8.31 J/mol/Kelvin)

According to Maxwell's

$$V_{RMS} = \sqrt{\frac{3P}{d}}$$

$$V_{MPS} = \sqrt{\frac{2P}{d}}$$

$$V_{avg} = \sqrt{\frac{8P}{\pi d}}$$

P = pressure (in Pascal)
 d = density (in kg/m^3)

Since $PM = dRT$

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

$$\boxed{V \propto \sqrt{\frac{T}{M}}}$$

[velocity depends on temperature & molar mass]

$$V_{RMS} = \sqrt{\frac{3(R/N_A)T}{M/N_A}}$$

$$= \sqrt{\frac{3KT}{\text{mass of one molecule (in kg)}}}$$

Some Important Points:

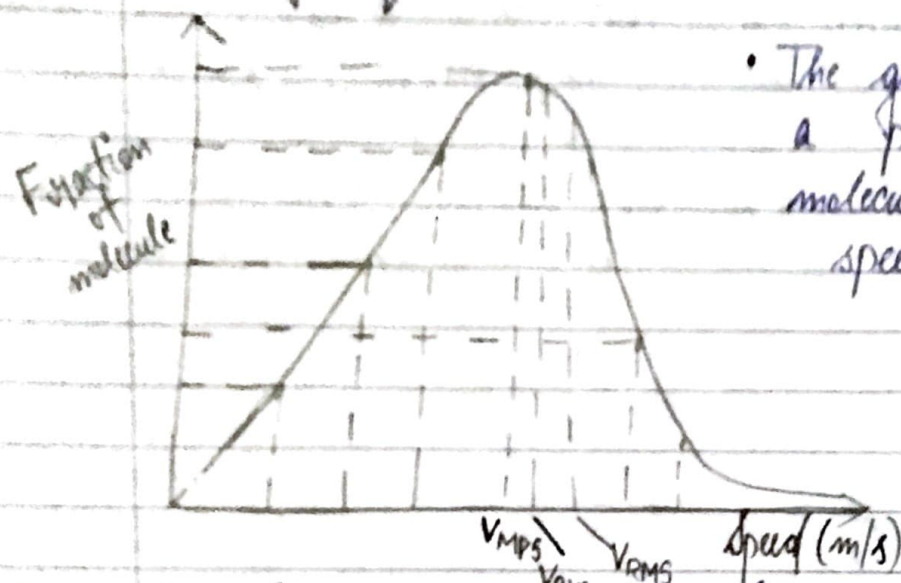
- At a particular temperature, a given gaseous molecule sample will have identical speed but the speed can be defined as V_{MPS} , V_{RMS} and V_{avg} .

0. Maxwell Distribution of Molecular Speed-

It was assumed that at a particular temperature, the molecules of a particular gas sample will have identical speed. This was not true, due to Brownian motion of the gaseous molecule.

According to Maxwell, for each range of ^{molecular} speed, there is

some molecule that exists which means a gaseous sample can have all type of molecular speed.



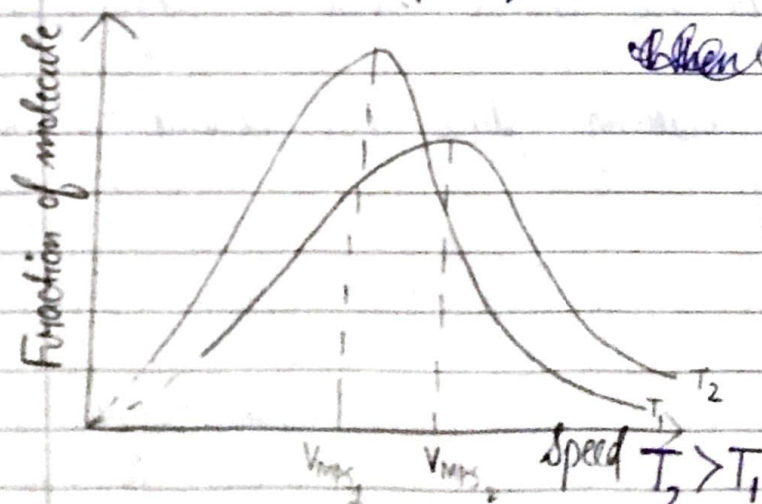
The given graph represent a particular fraction of molecule have particular speed.

The peak of the curve represent most probable speed.

$$V_{rms} : V_{avg} : V_{mps} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$$

Area under the curve represent total fraction of/number of molecule, which will remain constant.

When Maxwell curve is drawn for 2 different temperature, then the curve will get flatten.

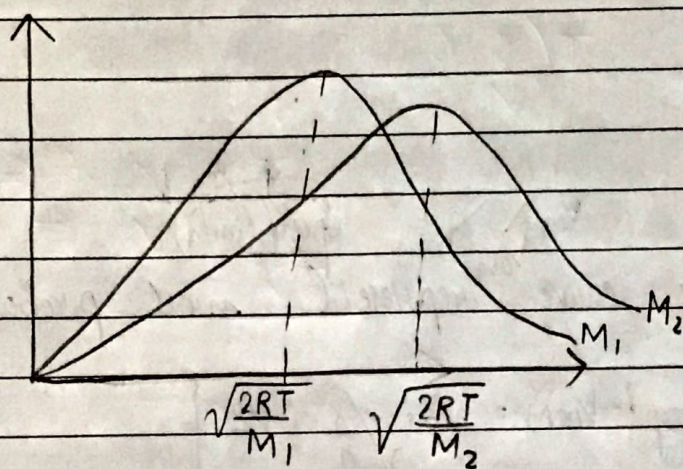


When 2 different

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- On increasing temperature, mole fraction belonging to lower speed range will decrease.
- Mole fraction belonging to v_{rms} will decrease but mole fraction belonging to higher speed range will increase.

Maxwell Distribution Curve for Two Different Gas:
(At particular temperature)



$$\text{As } \sqrt{\frac{2RT}{M_2}} > \sqrt{\frac{2RT}{M_1}} \quad [M_1 \text{ \& } M_2 \text{ are molar mass}]$$

$$(M_2 < M_1)$$

Collision Parameter:-

In collision parameter, we analyse collision frequency.

Number of collision taking place per second is known as collision frequency.

Collision frequency

Unimolecular

collision (Z_1)

Bimolecular

collision (Z_{11})

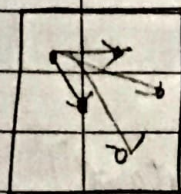
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Unimolecular collision:

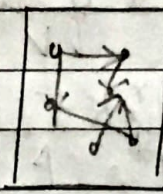
It is defined as no. of collision taking place by one molecule to other molecules. All remaining molecules are in rest.

Bimolecular collision:

In bimolecular collision, all molecules are considered to be in motion and collide with each other.



Let there be N molecules.



Let there be N molecules.

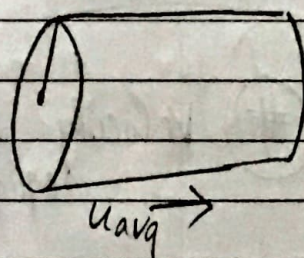
Unimolecular collision
Total no. of collision = $\boxed{N-1}$

Bimolecular collision
Total no. of collision = $\boxed{\frac{N^2}{2}}$

Collision volume -

Volume occupied between two successive collision.

Collision radius:
(σ)



Assume 2 molecule approach each other at right angle, and molecule can collide with any radial direction. So volume excluded in 1s:

collision volume = $\boxed{\pi \sigma^2 u_{avg}}$

$\boxed{\frac{1}{2} (1) (1) (1) = 1.5}$

Number Density -

Number of molecules present per unit volume is known as number density (N^*)

$$PV = nRT$$
$$\Rightarrow PV = \frac{\text{No. of molecules}}{N_A} RT$$

$$\Rightarrow P = \left(\frac{\text{No. of molecules}}{V} \right) \left(\frac{R}{N_A} \right) T$$

$$\Rightarrow P = N^* K T$$

$$\Rightarrow \boxed{N^* = \frac{P}{KT}} \quad [K = \text{Boltzman constant}]$$

No. of molecules present in collision volume =

$$\boxed{\pi \sigma^2 u_{\text{avg}} N^*}$$

Unimolecular collision (Z_1),

$$= \pi \sigma^2 u_{\text{avg}} N^*$$

$$= \boxed{\pi \sigma^2 u_{\text{avg}} \frac{P}{KT}}$$

(#) Velocity modification $\Rightarrow$

$$\text{Modified } u_{\text{avg}} = \sqrt{u_x^2 + u_y^2}$$
$$= \sqrt{2} u_{\text{avg}}$$

$$\boxed{Z_1 = \pi \sigma^2 (\sqrt{2} u_{\text{avg}}) \frac{P}{KT}}$$

$$Z_{11} = \pi \sigma^2 (\sqrt{2} u_{\text{avg}}) \left(\frac{N^*}{2} \right)^2$$

$$\boxed{Z_{11} = \pi \sigma^2 (\sqrt{2} u_{\text{avg}}) \left(\frac{P}{KT} \right)^2 \frac{1}{2}}$$

Some Important Points:

$$Z_1 \propto \left(u_{\text{avg}} \right) \frac{P}{T}$$

$$Z_1 \propto \sqrt{\frac{8RT}{\pi M}} \frac{P}{T}$$

$$\boxed{Z_1 \propto \frac{P}{\sqrt{T}}} \quad (\text{In general})$$

• At constant volume,
 $PV = nRT$
 $P \propto T$

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

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• At constant pressure,
 $Z_1 \propto \frac{u_{\text{avg}}}{T}$

$$Z_1 \propto \sqrt{\frac{8RT}{\pi M}} \left(\frac{1}{T} \right)$$

$$\boxed{Z_1 \propto \frac{1}{\sqrt{T}}}$$

• At constant temperature,
 $Z_1 \propto \frac{u_{\text{avg}}}{T} \frac{P}{T}$

$$Z_1 \propto \sqrt{\frac{8RT}{\pi M}} \left(\frac{P}{T} \right)$$

$$\boxed{Z_1 \propto P}$$

Bimolecular collision:

$$Z_{11} = \sqrt{2} n \sigma^2 u_{\text{avg}} \left(\frac{P}{KT} \right)^2 \frac{1}{2}$$

$$Z_{11} \propto u_{\text{avg}} \frac{P^2}{T^2}$$

$$Z_{11} \propto \sqrt{\frac{8RT}{\pi M}} \frac{P^2}{T^2}$$

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

At constant volume,
 $P \propto T$

$$P = kT$$

$$Z_{11} \propto \frac{k^2 T^2}{T^{3/2}}$$

$$\boxed{Z_{11} \propto T^{1/2}}$$

At constant pressure,

$$Z_{11} \propto \frac{1}{T^{3/2}}$$

At constant temperature,

$$Z_{11} \propto P^2$$

Mean Free Path (λ) -

Average distance travelled between two successive collision is known as mean free path.

$\sqrt{2}\pi\sigma^2 u_{avg} N^*$ collision took place in u_{avg} distance.
1 collision will take place in =

$$\frac{u_{avg}}{\sqrt{2}\pi\sigma^2 u_{avg} N^*}$$

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

$$\Rightarrow \lambda = \frac{KT}{\sqrt{2}\pi\sigma^2 P}$$

Note - For unimolecular collision, one molecule at rest & other is moving. Thus, distance b/w collision will be maximum.

• λ for bimolecular collision will always be ~~less~~ less than unimolecular collision.

Since, $\lambda \propto \frac{T}{P}$

At constant volume,

$$P \propto T$$

$$\lambda \propto \frac{T}{KT}$$

★ λ is independent of T and P .

• The K.E can be transferred from one molecule to another but it can not be converted into heat or any other form of energy.

• change in momentum in x direction

$$\Delta p_x = m(u - (-u)) = 2mu$$

• immediately after the collision, the molecule takes time equal to $\frac{d}{u}$ to collide with the opposite wall and time $\frac{2d}{u}$ to strike again with the same surface.

$$\frac{\Delta p_x}{\Delta t} = \frac{2mu}{(d/u)} = \frac{2mu^2}{d}$$

total change in momentum of the single molecule per unit time arising from collision is

$$\frac{\Delta p}{\Delta t} = \frac{2mu^2}{d} + \frac{2mv^2}{d} + \frac{2mw^2}{d}$$

$$= \frac{2m}{d} (u^2 + v^2 + w^2)$$

$$= \frac{2m}{d} c^2$$

for N molecule

$$= \frac{2mNc^2}{d}$$

Rate of change of momentum = force

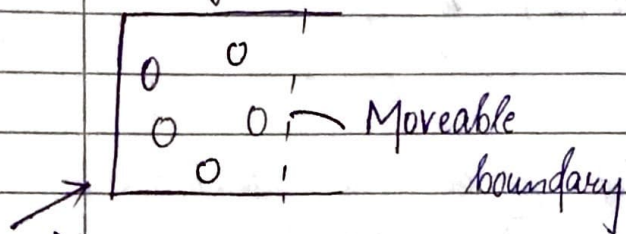
Pressure p

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Real Gas

When we consider ~~actual~~ interactive forces between the gaseous molecule and gaseous molecule are solid and hard sphere, then ~~ideal~~ gases behave like a real gas.

Actually, all gases are real gas but at low pressure & high temperature, it is considered as ideal gas.



$$V_{\text{container}} = V_{\text{occupied}} + V_{\text{ex}}$$

$\downarrow$ (volume available for movement) $\downarrow$ (volume of molecules)

When $P \downarrow$, $V_{\text{cont}} \uparrow$

$$V_{\text{container}} = V_{\text{occ}} + V_{\text{ex}}$$

When $V_{\text{cont}} \gg V_{\text{ex}}$

$$V_{\text{cont}} = V_{\text{occ}} \quad (\text{molecules are point mass})$$

At very high temperature, KE is very very high and PE can be neglected in comparison of KE. So, at high temperature, all types of interaction (either attractive or repulsive, i.e., PE) diminishes & hence the gas behave like an ideal gas.

$$TE = KE + PE$$

$T \uparrow$ $KE \uparrow$

$$KE \gg PE$$

$$TE = KE \quad [PE \Rightarrow \text{neglected}]$$

• It does not follow $PV = nRT$.

• Real gas is explained by the following theories:

- (i) Compressibility Factor theory
- (ii) Vanderwaal Gas theory

Compressibility Factor Theory-

$$\text{Compressibility factor } (Z) = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

(i) If $V_{\text{real}} > V_{\text{ideal}}$

$Z > 1$ [repulsive forces will dominate]
Gas is not easily liquefiable or compressible
as due to repulsive force, molecules can't be brought together.

Note - Strength of attractive force depends on molar mass & surface area.

(ii) If $V_{\text{real}} < V_{\text{ideal}}$, attractive

$(Z < 1)$ force will dominate

Directly proportional.

The gas is easily compressible & liquefaction is possible.

(iii) If $(Z = 1)$ $V_{\text{real}} = V_{\text{ideal}}$

Neither attractive nor repulsive forces will dominate.
Hence, gas behaves ideally.

Gas can be compressed easily but cannot be liquefied as attractive forces are absent.

$$PV_{\text{ideal}} = nRT$$

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

$$\Rightarrow V_{\text{ideal}} = \frac{V_{\text{real}}}{Z}$$

$$\boxed{PV_{\text{real}} = Z\eta RT} \quad \text{Real gas equation}$$

Q1) A 20L container consist 2g of gas at 300K, at a pressure of 2 atm. Predict the nature of gas & find out c.f value (Z).

$$PV = 2 \times 20$$

$$= 40$$

$$\eta RT = 2 \times \frac{1}{12} \times 300 = 50$$

Real gas as it does not follow eqⁿ.

$$40 = Z \cdot 50$$

$$\Rightarrow \boxed{Z = 0.8}$$

Q2) At 250K and 15 atm pressure, molar volume of gas is 12.1 smaller than ideal gas. Find out c.f value.

$$P = 15 \text{ atm}; T = 250 \text{ K}; \eta = 1$$

Ideally,

$$PV = \eta RT$$

$$\Rightarrow 15V = R \cdot 250$$

$$\Rightarrow V = \frac{250R}{15}$$

$$\text{Given, real vol.} = V - \frac{12.1}{100} V = \frac{88V}{100}$$

$$\frac{15 \times 88V}{100} = 1 \times R \times 250 Z$$

$$\Rightarrow \frac{15 \times 88}{100} \times \frac{250R}{15} = Z \cdot R \cdot 250$$

$$\Rightarrow \boxed{Z = 0.88}$$

Q3) Calculate the temperature of gas having molar mass 40g/mol, c.f. value (z) 1.2, density 1g/l and $P = 0.82 \text{ atm}$

$$PV_m = z \eta RT$$

$$\Rightarrow PV_m = z \frac{GM}{MM} RT$$

$$\Rightarrow P(MM) = z dRT$$

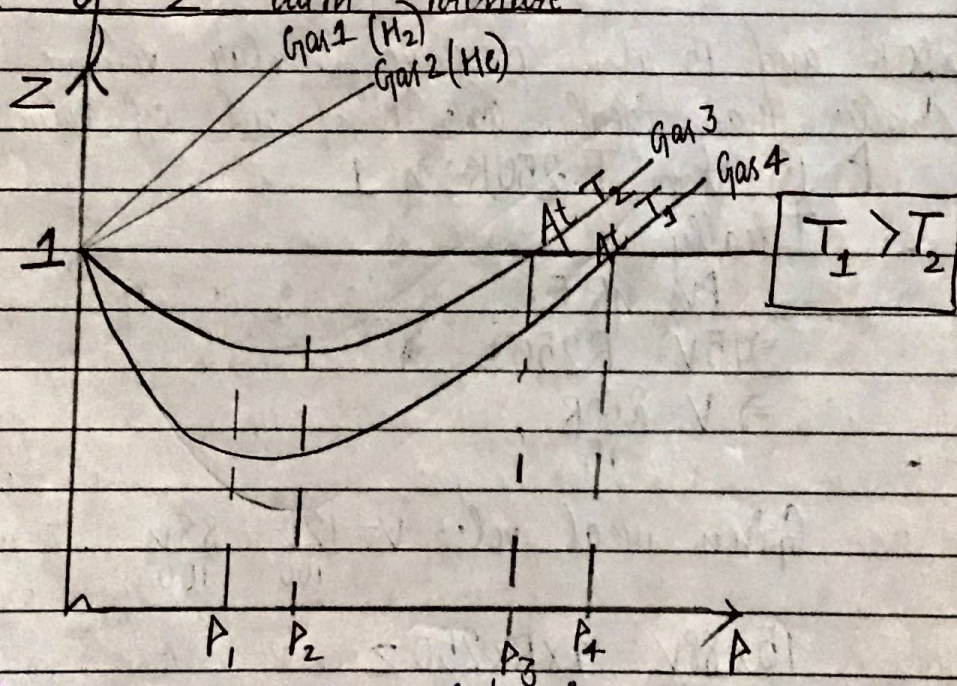
$$\Rightarrow 0.82 \times 40 = 1.2 \times 1 \times 0.0821 \times T$$

$$\Rightarrow \frac{8.2 \times 40}{1.2 \times 0.0821} = T$$

$$\Rightarrow \frac{10 \times 400}{12 \times 6} = T$$

$$\Rightarrow \frac{2000}{6} = 333.3 \text{ K} = T$$

Variation of ' z ' with Pressure -



• For gas 1 & gas 2, the value of z is always greater than 1 for all range of pressure. Hence, gas 1 and 2 cannot be liquefied.

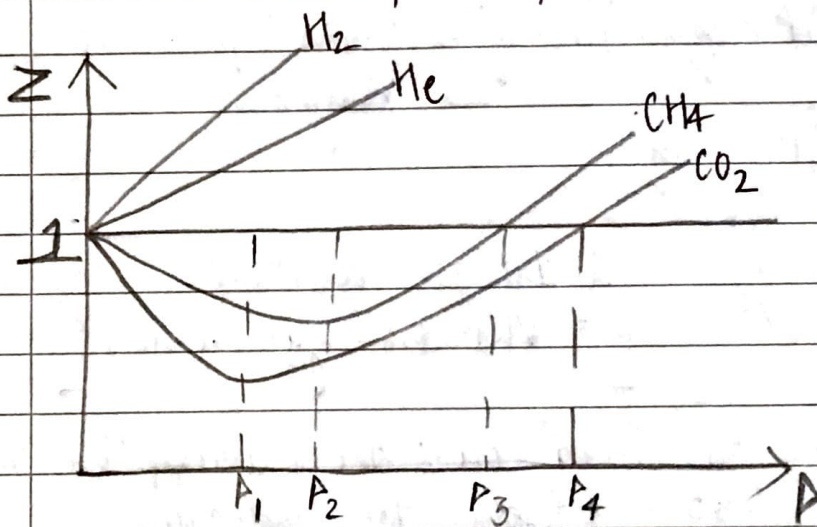
• Gas 2 is less steep than gas 1 means gas 2 is more

mean to $Z=1$. Hence, gas 2 ~~is~~ has less repulsive force means it can be easily compressed in comparison of gas 1.

Gas 3 can be liquified in pressure range of 0 to P_3 because in this pressure range value of Z is less than 1. At P_2 pressure, gas 3 can be liquified maximum and more easily.

The lowest peak of gas 4 lie below gas 3 which signifies that gas 4 has more attractive force than gas 3.

Higher the attractive force between the gaseous molecule, ~~lower~~ will be its ~~lowest~~ peak.
lower downward



At 'P' tends to zero, the gaseous molecule will behave like an ideal gas & cannot be liquified.

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Graph which ~~is parallel to~~ $Z=1$ & coincide with $Z=1$ behave like an ideal gas & cannot be liquified in any pressure range.

When Z versus P graph is drawn at 2 different temperature then the graph which is near to $Z=1$ will

have more ideal behaviour than other.

Vanderwaal's Theory -

Pressure Correction: $P_{ideal} V_{ideal} = nRT$

$$P_{ideal} > P_{real}$$

$$P_{ideal} = P_{real} + \Delta P$$

If attractive forces dominate in the molecule, then individual molecule cannot strike the wall of the container with max. capacity. So P_{real} will be less than P_{ideal} .

ΔP = Pressure correction factor

$$\Delta P \propto \left(\frac{n}{V}\right) \left[\begin{array}{l} \text{due to dependancy of number} \\ \text{of collisions} \end{array} \right]$$

$$\Delta P \propto \frac{n}{V} \left[\begin{array}{l} \text{no. of molecules per unit} \\ \text{volume} \end{array} \right]$$

$$\Delta P \propto \left(\frac{n}{V}\right)^2$$

$$\Delta P = a \frac{n^2}{V^2} \left[\begin{array}{l} a = 1^{st} \text{ gas constant} \\ = V_L N \text{ 1st gas constant} \end{array} \right]$$

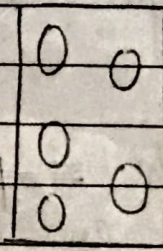
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Vanderwaal's Theory is based on the assumption that attractive forces dominate between the molecules.

Volume Correction:

$$V_{container} = V_{available} + V_{excluded/occupied}$$

$$V_{available} = V_{container} - V_{excluded/occupied}$$



Volume excluded by 2 molecules =

$$\frac{4\pi}{3} (2r)^3 = \frac{4\pi}{3} 8r^3$$



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$$\text{Volume excluded by 1 molecule} = \left(\frac{4\pi r^3}{3} \right) \frac{1}{2}$$

$$= 4 \times \frac{4\pi r^3}{3}$$

$$\text{Volume excluded by 1 mole} =$$

$$V_{ex} = \underbrace{4 \times \frac{4\pi r^3}{3} \times N_A}$$

b (2nd gas constant)

$$\text{Volume excluded by } n \text{ mole} = nb$$

$$V_{ideal} = V_{real} - nb$$

Overall gas equation,

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

Some Important Points:-

- 1st gas constant represent attractive forces between the gaseous molecules.
 - Unit of 1st gas constant is $\text{atm l}^2 \text{mol}^{-2}$.
 - In general, higher the molar mass or ~~volume~~ spherical surface, greater will be the value of a .
 - If Hydrogen bond is present in the molecule then higher the extent of Hydrogen bond, greater will be the value of a .
- e.g. $\text{NH}_3 > \text{C}_2\text{H}_6 > \text{CH}_4$
 $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$

- Higher the ~~value~~ molecular radius (all molecules are considered as solid sphere) greater will be the value of 'b'.
- 'b' represents volume or radius of molecule.
- The unit of 'b' is (Lit mol^{-1}) .

Modified form of Vanderwaal Gas equation -

(1)
$$\left(P + \frac{am^2}{V^2}\right)(V - nb) = nRT$$

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

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

$V_m = \text{molar volume}$
 $\text{Volume occupied by 1 mole}$

(2) At very high pressure,

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

$a \rightarrow 0$ [due to repulsive forces by high pressure attractive forces are negligible]

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

$$\Rightarrow PV_m - Pb = RT$$

$$\Rightarrow \frac{PV_m}{RT} - \frac{Pb}{RT} = \frac{RT}{RT}$$

$$\left[Z = 1 + \frac{Pb}{RT}\right] \quad (Z = \text{compressibility factor})$$

(3) At low pressure range,

At low pressure, volume of the container, i.e., V_{real} will be very high in comparison of excluded volume by the

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molecule. Hence, gaseous molecule can be considered as point mass.

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

$$r \rightarrow 0$$

$$b = 0$$

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

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

Dividing RT both sides,

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

$$\boxed{Z = 1 - \frac{a}{V_m RT}}$$

(4) At very high temperature & low pressure,

high temperature : $a \rightarrow 0$

low pressure : $b \rightarrow 0$

$$(P)(V_m) = RT$$

$$\Rightarrow (P)\left(\frac{V}{n}\right) = RT$$

$$\Rightarrow \boxed{PV = nRT}$$

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Vanderwall Gas Equation for Hydrogen & Helium -

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

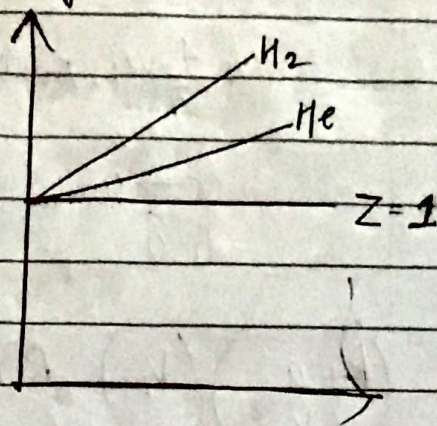
He, H_2 : $a \rightarrow 0$

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

$$\Rightarrow PV_M - Pb = RT$$

$$\Rightarrow \frac{PV_M}{RT} - \frac{Pb}{RT} = \frac{RT}{RT}$$

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



Drawbacks of Vanderwall Gas Equation -

- The equation works only for attractive force. To modify this, another equation was given that is known as Virial equation.

$$Z = 1 + \frac{B}{V_M} + \frac{C}{V_M^2} + \frac{D}{V_M^3} + \dots \quad [V_M \Rightarrow \text{molar volume}]$$

Every gas equation will follow the given Virial equation.

Vanderwall gas equation will also follow the Virial equation where B, C and D are 2nd, 3rd and 4th Virial co-efficients respectively.

- The Vanderwall gas equation can be written as per the Virial equation and 2nd, 3rd and 4th Virial co-efficient can be calculated for Vanderwall gas.

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

$$\Rightarrow P + \frac{a}{V_m} = \frac{RT}{V_m-b}$$

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

$$\Rightarrow \frac{PV_m}{RT} + \frac{a}{V_m RT} = \frac{1}{1-b/V_m}$$

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

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots \dots \dots \left. \begin{array}{l} \text{if } 0 < x < 1 \\ [x \text{ has very less value}] \end{array} \right\} \text{Virial eq}^n$$

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

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

★ When ~~B, C, D, ... are zero~~ $\left(\frac{b-a}{RT}\right), \left(\frac{b^2}{V_m^2}\right), \left(\frac{b^3}{V_m^3}\right) \dots \dots \dots$ is zero,
 $Z = 1$ [gas will behave ideally] $\left[B = \frac{b-a}{RT}\right]$

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

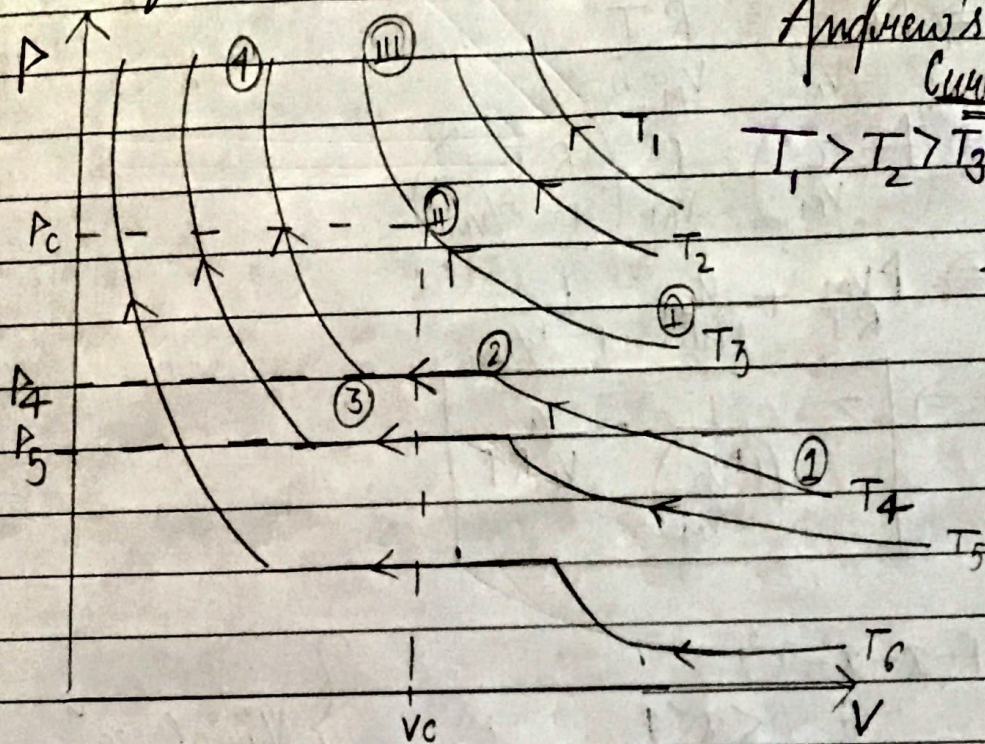
$$\Rightarrow \boxed{T = \frac{a}{bR}}$$

⇒ Boyle's temperature —
 Temperature at which gas behaves ideally.

[Calculated by 2nd Virial co-efficient]

★ When the second virial co-efficient is zero, then Boyle's temperature is calculated.

Liquification of Gas-



Andrew's Isotherm
Curve

$$T_1 > T_2 > T_3 > T_4 > T_5 > T_6$$

- The curve represent liquification of a particular gas at different temperature.
- At higher temperature (T_1 or T_2), liquification of gas is not possible at any pressure range means we will get a continuous curve of 'P versus V'.
- At temperature T_3 , pressurizing the gas it follow continuous curve except at (V_c, P_c)
- At point V_c and P_c , first drop of liquid is formed.
- Region ~~(I) & (III)~~ represent (I) to (II) represent gas, at point (II) is discontinuous part also known as critical point. From region (II) to (III) represent gas.

Characteristic of critical point:

(1) 1st drop of liquid is formed but point II is thermo-neutral ($\Delta H = 0$: no exchange of energy). It should have been -ve, i.e., $\Delta H = -ve$. Also, surface tension = 0.

(2) T_c is known as critical temperature, and the value of T_c is $\frac{8a}{27Rb}$.

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

(3) The temperature above which gas cannot be liquified at any pressure range is known as critical temperature.

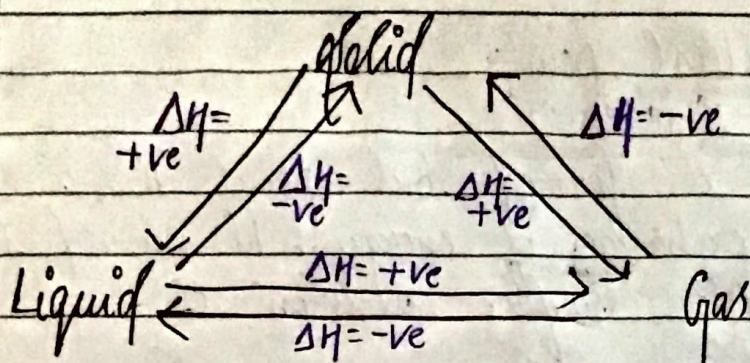
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• Region II to III represent gaseous state and known as super critical fluid.

• At point II, surface tension is zero as no droplet is formed at this point. With the help of critical temperature value of critical pressure & critical volume is calculated.

$$P_c = \frac{a}{27b^2} \quad V_c = 3b$$

• At temperature T_c , when we start pressurising the gas, liquification start at point P (2) and at point (3). Point (1) to (2) represent gas. Point (2) to (3) represent phase transformation (gas $\Rightarrow$ liquid) ($\Delta H = -ve$)



$\Delta H = +ve$: Endothermic (energy absorbed)

$\Delta H = -ve$: Exothermic (energy released)

- Pressure corresponding to the phase transformation is known as vapour pressure. At T_4 temperature, vapour pressure will be P_4 .
- Region (3) to (4) represent liquified gas which does not change their volume significantly, after heavy compression.
- At temperature T_5 , ~~since~~ T_5 temperature is lower than T_4 , on compressing the gas, liquification will start early & will go longer in comparison of T_4 .
- Higher the value of critical temperature, more easily the gas can be liquified. Higher the value of 'a', greater will be its critical temperature, i.e., higher the value of attractive forces, greater will be its value of 'a'.