300

12/8/22

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Gaseous State

Temperature

Unit : K, °C, F

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

Volume

Unit: m^3, l, cm^3, ...

$1\ m^3 = 1000\ l$
$1\ cm^3 = 1\ ml$

Pressure

Unit : atm, mm Hg, torr, Pa, ...

1 atm = 760 mm Hg = 76 cm Hg = 760 torr
= $1.013 \cdot 10^5$ Pa

1 bar = 0.987 atm

Gas Laws

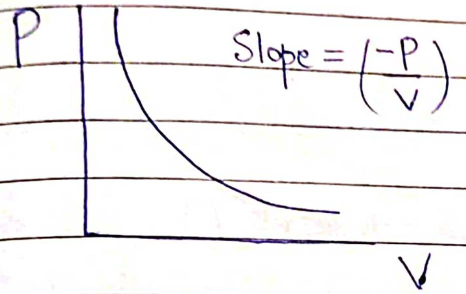
Boyle's Law Charle's Law GayLussac's Law

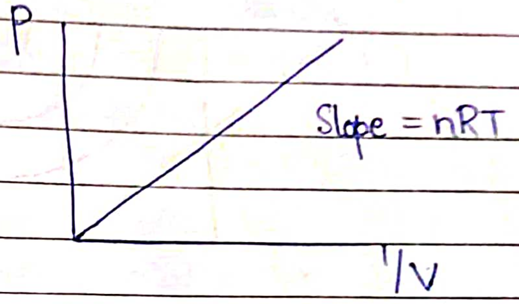
Avagadro's Law Dalton's Law

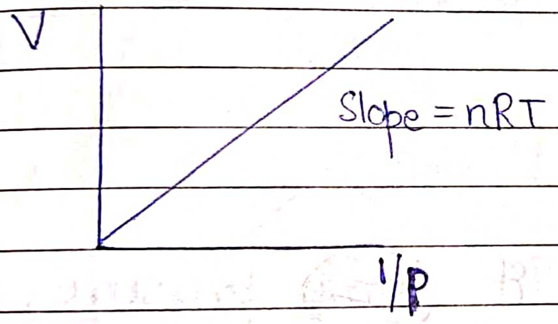
i) Boyle's Law : (T const.)

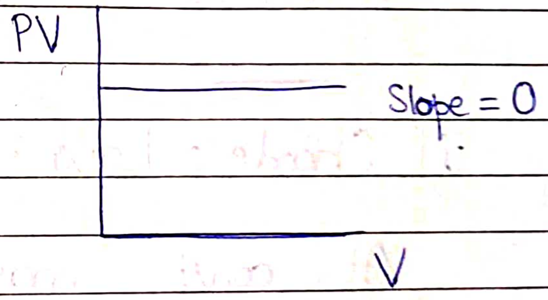
At const. mass and temp, $\boxed{\left(\text{vol of gas}\right) \propto \left(\frac{1}{\text{Pressure}}\right)}$

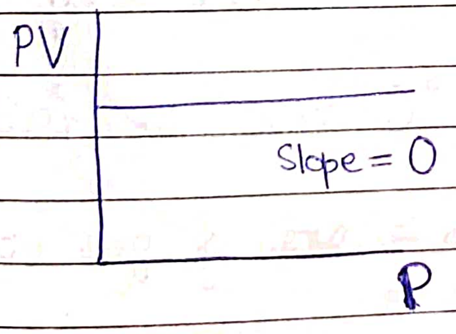
$\Rightarrow \boxed{PV = \text{Const.}}$

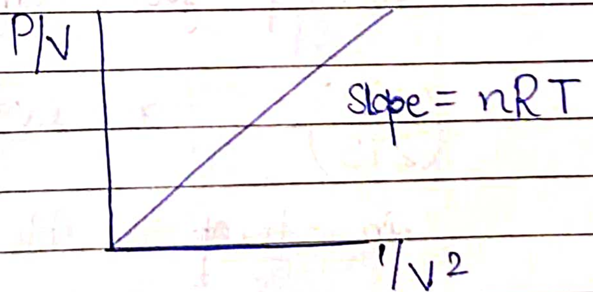


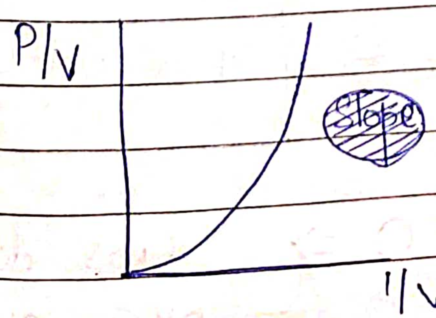


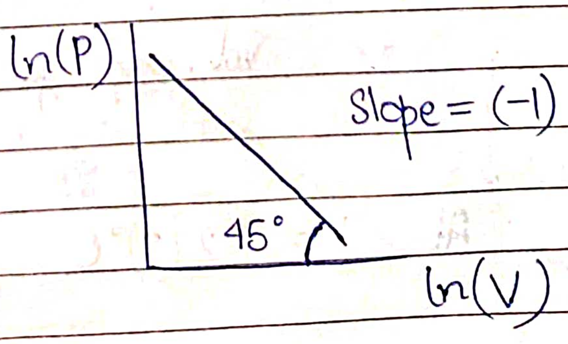


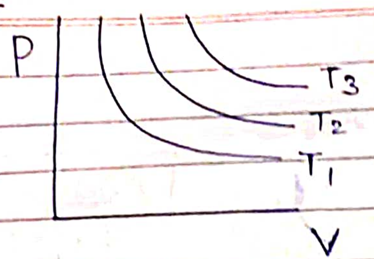






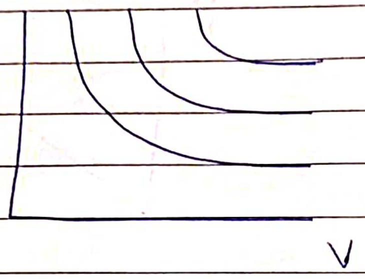




Q) 

Compare T_1, T_2, T_3.

A) Pick a const. V.



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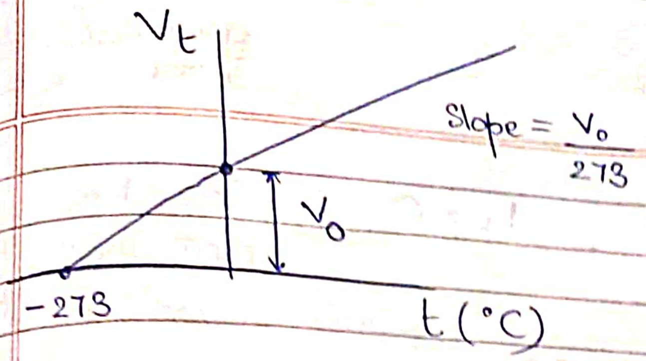
ii) Charle's Law : (P const.)

At const. mass & ~~temp~~ pressure, vol. of gas inc. or dec. by $\left(\frac{V_0}{273}\right)$ for every 1 °C rise or fall in temp. Here, V_0 = vol. of gas at 0°C

⇒ Vol. of gas at t°C ⇒ $\boxed{V_t = V_0 + \frac{tV_0}{273}}$

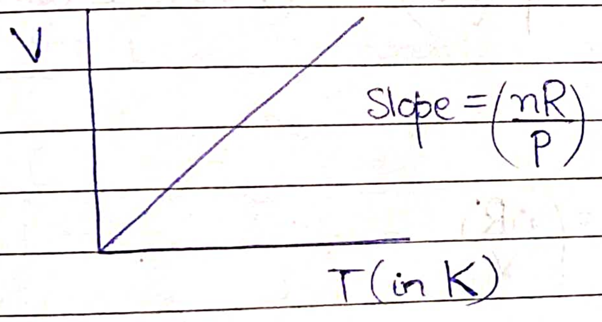
At $t = (-273)°C$, $V_t = 0$ ⇒ Gas does NOT exist.



$$V_t = V_0\left(1+\frac{t}{273}\right) = \left(\frac{V_0}{273}\right)(273+\overset{\text{in °C}}{t}) = \left(\frac{V_0}{273}\right)(\overset{\text{in K}}{T})$$

$$\Rightarrow \boxed{V \propto T}$$

Hence, Charle's Law can also be defined as — At const. mass & pressure, $\boxed{(\text{vol. of gas}) \propto (\text{Absolute temp.})}$

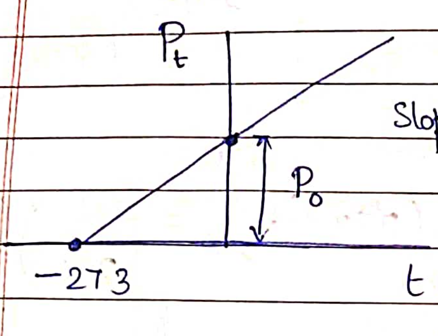


iii) Gay Lussac's Law : (V const.)

At const. mass & vol., pressure of gas inc. or dec. by $\left(\frac{P_0}{273}\right)$ for every 1°C rise or fall in temp. Here, P_0 = pressure of gas at 0°C

⇒ ~~Vol~~ Pressure of gas at t°C ⇒ $\boxed{P_t = P_0 + \frac{tP_0}{273}}$

At $t = (-273)°C$, $P_t = 0 \Rightarrow$ Gas does NOT exist.

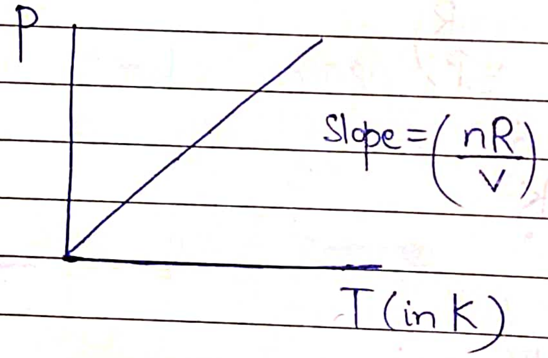


$$P_t = P_0\left(1 + \frac{t}{273}\right)$$

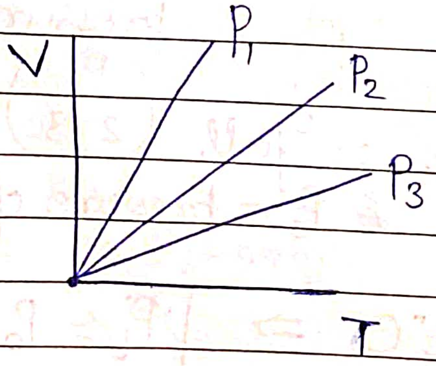
$$= \left(\frac{P_0}{273}\right)\underbrace{(273+t)}_{\text{in °C}} = \left(\frac{P_0}{273}\right)\underbrace{T}_{\text{in K}}$$

$$\Rightarrow \boxed{P \propto T}$$

Hence, Gay Lussac's Law can also be defined as — At const. mass & vol., $\boxed{(\text{pressure of gas}) \propto (\text{Absolute temp.})}$



Q) Compare P_1, P_2, P_3

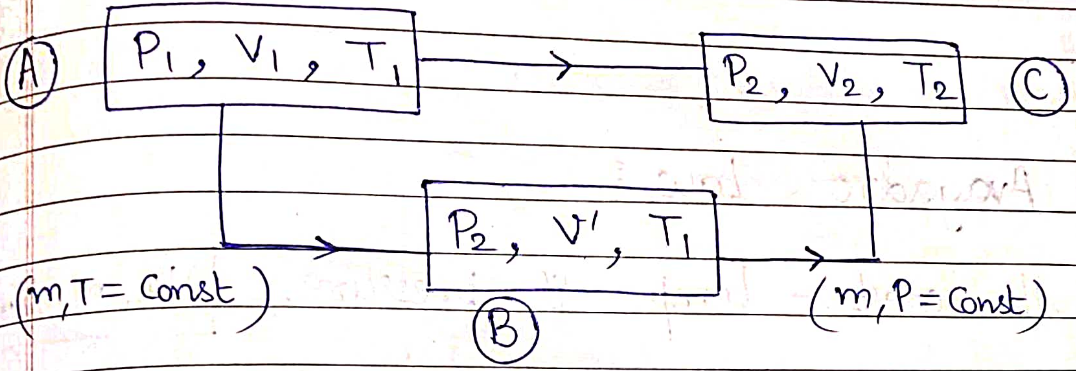


A) Slope $= \left(\frac{nR}{P}\right)$

$$\Rightarrow \boxed{P_3 > P_2 > P_1}$$

iv) Ideal Gas Eqn:

Let m = Const.



A → B, Boyle's Law ⇒ $P_1 V_1 = P_2 V'$

B → C, Charle's Law ⇒ $\frac{V'}{T_1} = \frac{V_2}{T_2}$

$$\Rightarrow \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \boxed{\frac{PV}{T} = \text{Const.}}$$

By Avagadro's Law

For 1 mol, $\frac{PV}{T} = R$ ⇒ for n mol, $\frac{PV}{T} = nR$

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

V — Vol. available for free movt of gas.

Significance of R:

$$\boxed{R = \left(\frac{PV}{nT}\right) = \left(\frac{\text{Energy}}{\text{mol } K}\right)}$$

Amt. of work (energy) obtained ~~by~~ from 1 mol gas when temp. raised by 1K.

$R = 2 \frac{cal}{mol\,K}$

$R = 0.0821 \frac{atm\,L}{mol\,K} = \frac{1}{12} \frac{atm\,L}{mol\,K}$

$R = 8.314 \frac{J}{mol\,K} = \frac{25}{3} \frac{J}{mol\,K}$

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v) Avagadro's Law : (T, P const.)

At const. temp. & pressure, $\boxed{Vol. \propto (\# mol)}$

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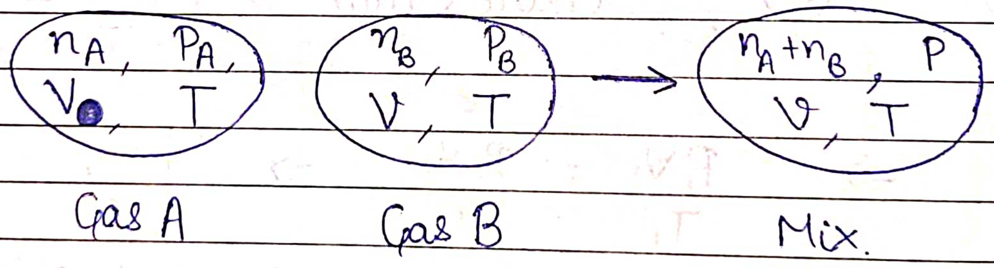
vi) Dalton's Law (of partial pressures) :

Applicable only for non reacting gases.



$P_A V = n_A RT$ $P_B V = n_B RT$ $PV = (n_A+n_B)RT$

Under similar condition of temp. & vol., total pressure exerted by mix. of non reacting gases is equal to sum of partial pressure of all gas.

$\boxed{P = P_A + P_B}$

P_A – Partial pressure of A.

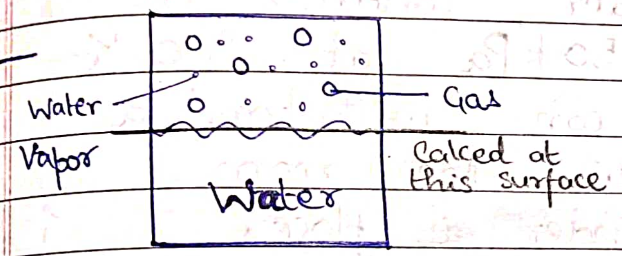
P_B – Partial pressure of B.

Now, $\left(\frac{P_A V}{PV}\right) = \left(\frac{n_A}{n_A + n_B}\right) \Rightarrow \boxed{P_A = P\chi_A}$

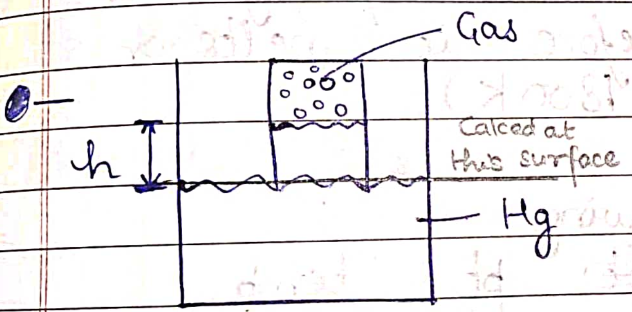
Similarly, $\boxed{P_B = PX_B}$

X_A = Mol. fraction
X_B - Mol. fraction

- Collection of gas over surface of volatile liquid

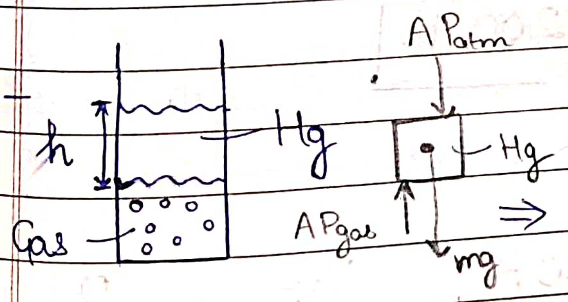


$$\boxed{P_{\text{wet gas}} = P_{\text{dry gas}} + \underbrace{P_{H_2O}}_{\text{Aq. tension}}}$$



$$\boxed{\underbrace{\overset{\text{(in atm)}}{P_{atm}}}_{\text{Pressure due to atmosphere.}} = \overset{\text{(in atm)}}{P_{gas}} + \underbrace{\overset{\text{(in atm)}}{\rho g h}}_{\text{Pressure due to Hg.}}}$$

- Calc. length of gas column trapped in liq.

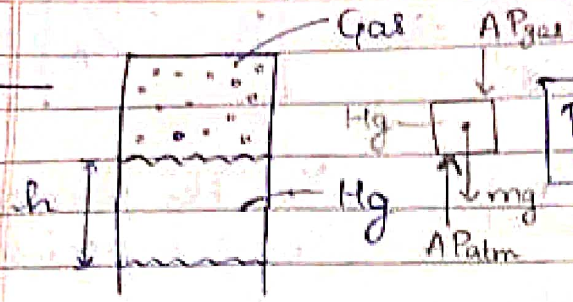


$P_{gas} > P_{atm}$

$$\boxed{P_{gas} = h + P_{atm}}$$

(in mm of Hg)

$$\boxed{\rho_{Hg} = 13.6 \text{ g cm}^{-3}}$$



$$\boxed{P_{atm} = P_{gas} + h}$$

(in mm of Hg)

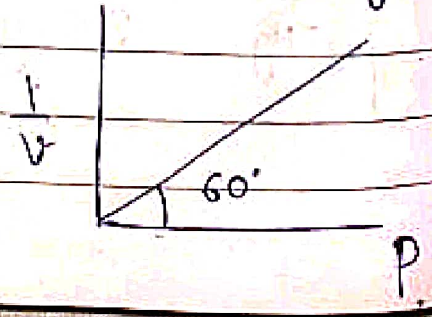
Q) An iron cylinder contains He at pressure 250 kPa at 300 K. The cylinder can withstand a pressure of 10^6 Pa. The room in which cylinder is placed catches fires. Predict if cylinder will blow up before it melts or not. (Melt. pt. = 1800 K)

A) Let T be ~~melt~~ blowing pt. temp.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{250 \cdot 10^3}{300} = \frac{10^6}{T}$$

$$\Rightarrow \boxed{T = 1200\ K}$$

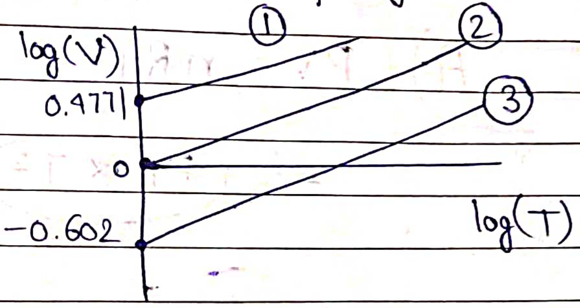
Q) At const. temp 300 K, $1/V$ vs P graph is plotted for an ideal gas. Find mol of gas.



A) $\text{Slope} = \frac{1}{PV} = \frac{1}{nRT} \Rightarrow \sqrt{3} = \frac{1}{300nR} \Rightarrow \boxed{n = \frac{1}{300\sqrt{3}R}}$

Q) At const. pressure 0.0821 atm, log(V) vs log(T) plotted for 3 samples of gas as shown.

Find out no. of moles in sample.



A) At $T = 1\text{ K}$, $\log(T) = 0$.

$\Rightarrow \log(V_1) = 0.4771, \quad \log(V_2) = 0, \quad \log(V_3) = -0.602$

$\Rightarrow V_1 = 3\text{ L}, \quad V_2 = 1\text{ L}, \quad V_3 = \frac{1}{4}\text{ L}.$

We have, $PV = nRT \Rightarrow (0.0821\text{ atm})\,V = n\left(0.0821 \frac{\text{atm L}}{\text{mol K}}\right)(1\text{ K})$

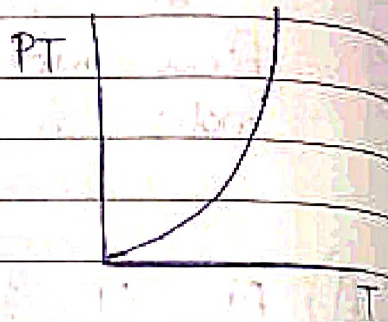
$\Rightarrow \boxed{n = V \frac{\text{mol}}{\text{L}}}$

$\Rightarrow \boxed{n_1 = 3\text{ mol}} \quad \boxed{n_2 = 1\text{ mol}} \quad \boxed{n_3 = \frac{1}{4}\text{ mol}}$

Q) Plot PT vs T graph for an ideal gas at const. vol. and moles. Find moles of gas taken, when vol. of vessel is 8.21 L and rate of change of PT = 800 at 400 K wrt T.

A) $PV = nRT \Rightarrow PT = \left(\frac{nRT^2}{V}\right)$

$\Rightarrow \boxed{PT \propto T^2}$ (Const V & n)



$$\frac{d}{dT}(PT) = \frac{d}{dT}\left(\frac{nRT^2}{V}\right) = \left(\frac{nR}{V}\right)\frac{d(T^2)}{dT}$$

$$\Rightarrow 800 = \frac{n(0.0821)}{(8.21)}(2\cdot400) \Rightarrow \boxed{n = 100}$$

Diffusion & Effusion

Diffusion : Mixing of gases due to collision and movement of gas molecules.

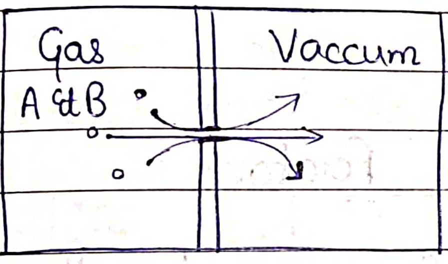
Effusion : It is process in which gas under high pressure escapes out from orifice of vessel.

v) Graham's Law (of diffusion):

- At const. P & T, $\boxed{(V.D.)_A = (11.2)\rho_A}$

$$\boxed{r_A = \left(\begin{matrix}\text{Rate of Diffusion}\\ \text{\& Effusion}\end{matrix}\right) \propto \frac{1}{\sqrt{(V.D)_A}} \propto \underbrace{\frac{1}{\sqrt{M_A}}}_{\text{Molar Mass}} \propto \underbrace{\frac{1}{\sqrt{\rho_A}}}_{\text{Density}}}$$

For 2 gases, $\boxed{\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}}$

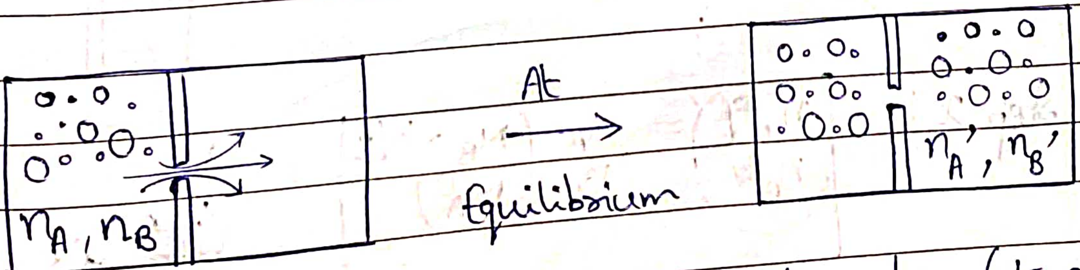


$$\left(\begin{matrix}\text{Rate of Diffusion}\\ \text{or Effusion}\end{matrix}\right) = \frac{\overset{\text{diffused}}{V}}{t}$$

$$\Rightarrow \text{effused} \left(\frac{V_A/t_A}{V_B/t_B}\right) = \sqrt{\frac{M_B}{M_A}}$$

If $t_A = t_B$ (time taken for both gases same).

$$\Rightarrow \boxed{\frac{V_A}{V_B} = \sqrt{\frac{M_B}{M_A}} = \frac{n_A}{n_B}} \text{ effused}$$

- 

If $P \neq$ const., but $t_A = t_B$ (time)
and $T =$ const.

v) Graham's Law (of diffusion):

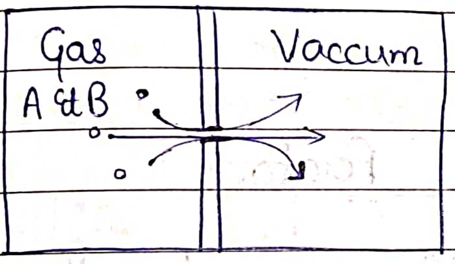
- At const. P & T,

$$\boxed{(V.D.)_A = (11.2)\,\rho_A}$$

$$\boxed{r_A = \left(\begin{array}{c}\text{Rate of Diffusion}\\ \text{\& Effusion}\end{array}\right) \propto \frac{1}{\sqrt{(V.D)_A}} \propto \frac{1}{\underbrace{\sqrt{M_A}}_{\text{Molar Mass}}} \propto \frac{1}{\underbrace{\sqrt{\rho_A}}_{\text{Density}}}}$$

For 2 gases,

$$\boxed{\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}}$$

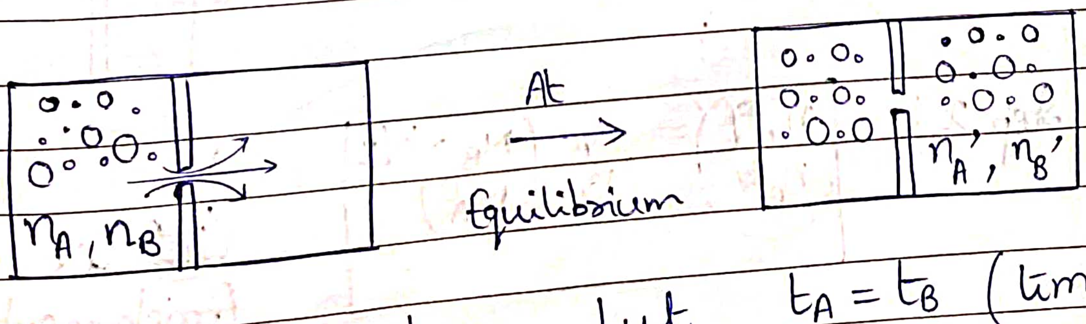


$$\left(\begin{array}{c}\text{Rate of Diffusion}\\ \text{or Effusion}\end{array}\right) = \frac{\overset{\text{diffused}}{V}}{t}$$

$$\Rightarrow \text{effused}\left(\frac{V_A/t_A}{V_B/t_B}\right) = \sqrt{\frac{M_B}{M_A}}$$

If $t_A = t_B$ (time taken for both gases same).

$$\Rightarrow \boxed{\frac{V_A}{V_B} = \sqrt{\frac{M_B}{M_A}} = \frac{n_A}{n_B}} \text{ — effused}$$

- 

If $P \neq$ const., but $t_A = t_B$ (time)
and $T =$ const.

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$$r \propto \frac{P}{\sqrt{M}} \Rightarrow \boxed{\frac{r_A}{r_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}}}$$

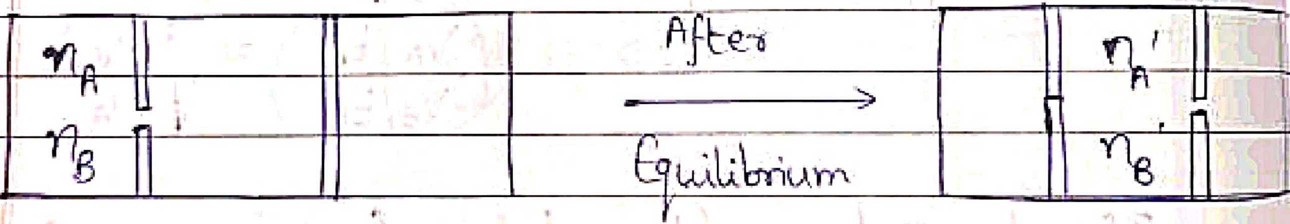
By Dalton's law, $\frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{x_A}{x_B} = \frac{W_A}{W_B} \cdot \frac{M_B}{M_A}$

Now, $\frac{r_A}{r_B} = \frac{n'_A/t_A}{n'_B/t_B} = \frac{n'_A}{n'_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}}$

$$\Rightarrow \boxed{\frac{n_A'}{n_B'} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}}}$$

effused — Initial

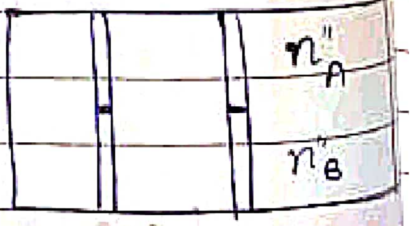
Enrichment / Seperation factor



Step 1 : $\frac{n_A'}{n_B'} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}} = \frac{n_A}{n_B}\left(\frac{M_B}{M_A}\right)^{1/2}$

After Equilibrium

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



⋮

Step x :- $\boxed{\frac{n_A^f}{n_B^f} = \frac{n_A}{n_B}\left(\frac{M_B}{M_A}\right)^{x/2}}$

~~x~~ is called Enrichment factor.

☆ If P, T, ≠ const. ⇒ $\boxed{r \overset{\propto}{=} \frac{PA}{\sqrt{2\pi MRT}}}$

A - Cross section area.

Effusion

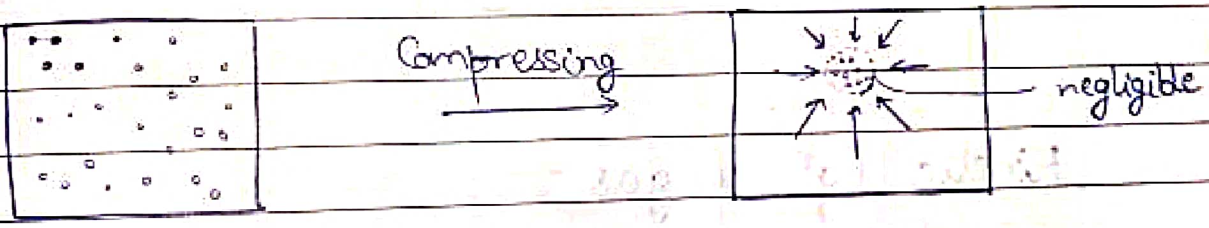
Kinetic Theory of Gases

Postulates -

1) Gas consist of tiny particles called molecules.

2) Motion of molecules is rapid & random. (Brownian Motion)

☆3)



Vol. occupied by gas molecules negligible compared to vol. of container.

$$\Rightarrow \boxed{V_{\text{free movt.}} \approx V_{\text{container}}}$$

☆4) There are no intermolecular forces among gas molecules. (Potential Energy = 0)

i.e. $\boxed{\text{Total Energy} = \text{Kinetic Energy}}$

3|4

5) Gas molecules travel in a strt line and change dirxn on collision

6) Collisions among molecules assumed to be perfectly elastic.

7) Pressure of gas only due to striking of gas molecules on walls of container.

8) There is no effect of gravity on gas molecules.

9) (K.E. of particles) ∝ (Absolute Temp.).

Kinetic Eqn of gas —

(Practical)

$$\boxed{PV = \frac{1}{3} m N v_{rms}^2}$$

P - Pressure by gas
V - Vol. of container
m - Mass of 1 particle
N - No. of particles.

v_{rms} - Root Mean Sq. vel.

$$\boxed{v_{rms} = \sqrt{\frac{v_1^2 + \dots + v_N^2}{N}}}$$

K.E. of gas molecule -

$$T.E. = K.E. = \frac{1}{2}mv_1^2 + \ldots + \frac{1}{2}mv_N^2$$

$$= \frac{1}{2}m\left(v_1^2 + \ldots + v_N^2\right)$$

$$\Rightarrow \quad K.E. = \frac{1}{2}mNv_{rms}^2 \Rightarrow \boxed{KE = \frac{3PV}{2}}$$

for 1 mol ideal gas $\Rightarrow$ $KE = \frac{3}{2}RT$

for n mol ideal gas $\Rightarrow$ $\boxed{KE = \frac{3}{2}nRT}$

for 1 gas particle $\Rightarrow$ $KE = \frac{3}{2}\frac{R}{N_A}T$ -

$$\Rightarrow \boxed{KE = \frac{3}{2}k_bT}$$

Boltzmann Const.

$$\boxed{k_b = 1.38 \cdot 10^{-23}\ J/K}$$

Root Mean sq. vel -

We have, $K.E. = \frac{1}{2}mNv_{rms}^2$

for n mol ideal gas, $\frac{3}{2}RTn = \frac{1}{2}Mv_{rms}^2 n$

Molar Mass of gas.

$$\Rightarrow \boxed{v_{rms} = \sqrt{\frac{3RT}{M_{gas}}}}$$

Molar Mass.

In $v_{rms} = \sqrt{\frac{3RT}{M_{gas}}}$,

$$PV = nRT = \left(\frac{W}{M_{gas}}\right)RT \Rightarrow PM_{gas} = \left(\frac{W}{V}\right)RT$$

$$\Rightarrow \rho = \frac{PM_{gas}}{RT} \Rightarrow \boxed{\frac{RT}{M_{gas}} = \frac{P}{\rho}}$$

$$\Rightarrow \boxed{v_{rms} = \sqrt{\frac{3P}{\rho}}}$$

Maxwell's Distr. of Molecular Speed –

Assumption: Same as K.T.G.

Imp. Pts:

1) It is impossible to track speed variation of an individual gas molecule as it collides with molecules billions of times or even more per second.

2) Since pressure, temp., K.E., ... of a gas system remains const. with time if undisturbed, hence fraction of gas molecules having speed in range should const. at a given temp.

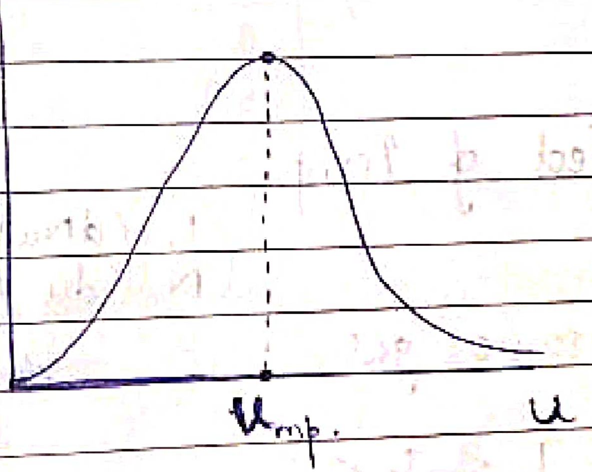
3) Mathematically, Maxwell derived an eq^n from statistical approach from a large collection of gas molecules.

$$\boxed{dN_u = 4\pi N\left(\frac{M}{2RT\pi}\right)^{3/2} e^{-\frac{Mu^2}{2RT}} u^2\,du}$$

This describes distr. of molecular speed

N - No. of gas molecules
M - Molar Mass of gas
dN_u - No. of gas molecules with speed $\in [u, u+du]$
$\left(\frac{dN_u}{N}\right)$ - Fraction " " " " " " "

V_{mp} - Most Probable Speed



$$\Rightarrow \boxed{V_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2P}{\rho}}}$$

Features :

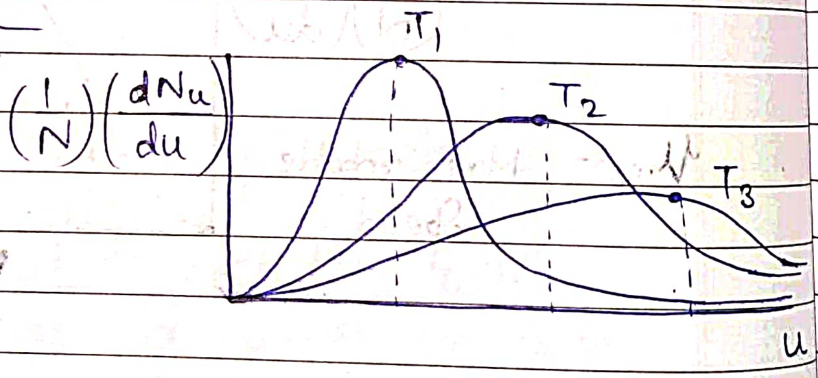
1) No. of gas molecules having either very high vel. ~~of~~ or very low vel. is small.

2) Most particles have speed near V_{mp}.

3) Area under $\left(\frac{1}{N}\right)\left(\frac{dN_u}{du}\right)$ vs u graph is const., and equal to $\boxed{1}$.

4) Area under $\left(\frac{dN_u}{du}\right)$ vs u graph is const., and equal to $\boxed{N}$.

5) Effect of Temp. –



For same gas,

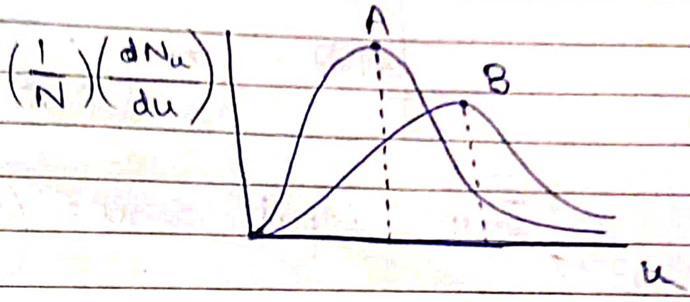
$T_1 < T_2 < T_3$

6) By inc. in temp,

$V_{mp}\uparrow$, $\left(\text{fraction of particles with } V_{mp}\right)\downarrow$, $\left(\#\text{ particles with low speed}\right)\downarrow$, $\left(\#\text{ particles with high speed}\right)$

7) Speed distr. also depend on Molar Mass of gas.

for same temp.



Molar Mass : B < A

as $v_{rms} \propto M^{-1/2}$.

8) Maxwell distr. curve of 2 gases same if v_{rms} of both same

$$\Rightarrow \boxed{\frac{T_A}{M_A} = \frac{T_B}{M_B}}$$

(formula valid for large no. of molecules)

Types of Speed (of gas particles) —

1) Root Mean Sq. Vel : $\boxed{V_{\cancel{mp}\,rms} = \sqrt{\frac{3RT}{M}}}$

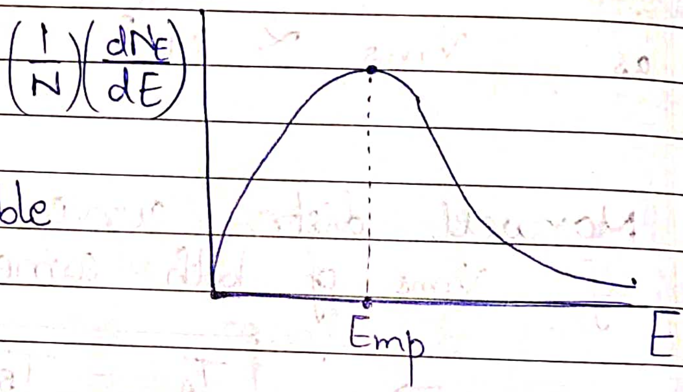
2) Average Vel. : $\boxed{V_{avg} = \sqrt{\frac{8RT}{\pi M}}}$ $\left(\frac{v_1 + \ldots + v_N}{N}\right)$

3) Most Probable Vel. : $\boxed{V_{mp} = \sqrt{\frac{2RT}{M}}}$

Maxwell's Distr. of K.E. —

$$\boxed{dN_E = 2\pi N\left(\frac{1}{RT\pi}\right)^{3/2} e^{-\frac{E}{RT}} \sqrt{E}\, dE}$$

Just input $u = \left(\frac{2E}{m}\right)^{1/2}$ in earlier formula



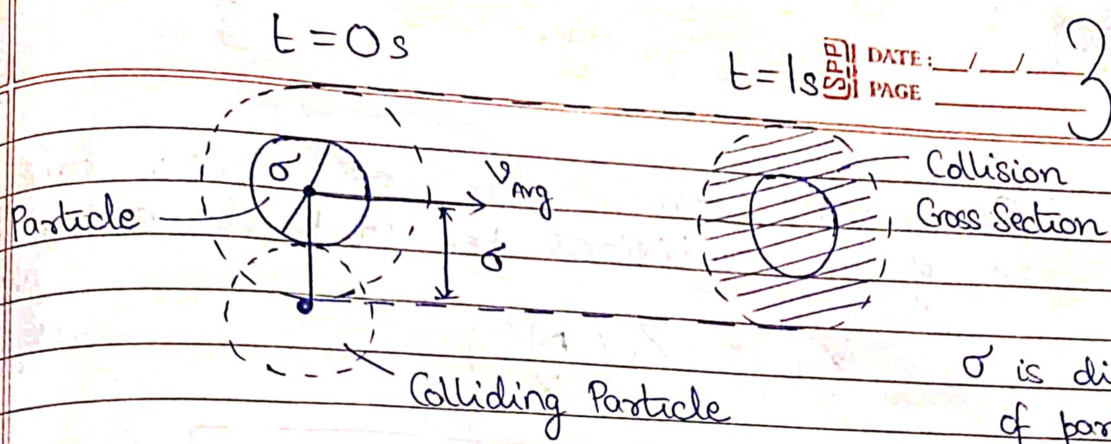
Emp – Most Probable Energy

$\Rightarrow$ $\boxed{E_{mp} = \frac{1}{2} RT}$

Collision Freq. & Mean Free Path

Collision Freq. (Z_{11}): Total no. of collisions b/w similar molecules per unit vol. per unit time.

Assumptions: 1) All particles have same size & shape spherical
2) Vel. of all particles = v_{Avg}.



σ is diameter of particle

$$\begin{pmatrix}\text{Vol. swept} \\ \text{in 1s}\end{pmatrix} = \pi\sigma^2 u_{Avg}.$$

Consider all other particles at rest.

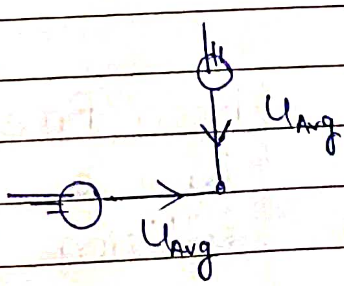
Let $N^* = \frac{N}{V}$, i.e. $\begin{pmatrix}\text{\# particles per} \\ \text{unit vol.}\end{pmatrix}$.

$$\Rightarrow \begin{pmatrix}\text{No. of molecules} \\ \text{colliding with particle}\end{pmatrix} = \pi\sigma^2 u_{Avg} N^*$$

In reality, all molecules <u>NOT</u> stationary. They all hit a diff. angles.

Since angle of collision $\in [0, 180^\circ]$

We assume all hit at 90°. and take vel. rel



$$\Rightarrow \boxed{Z_1 = \pi\sigma^2 u_{Avg}\sqrt{2}\, N^*}$$

$\begin{pmatrix}\text{\# collisions by} \\ \text{a particle per unit time}\end{pmatrix}$

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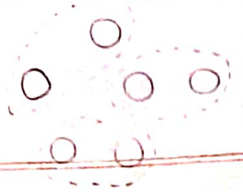


N particles

⇒ (N/2) bimol collisions per unit time

Considering bimolecular collisions, total no. of collisions per unit time per unit vol.

$$Z_{11} = Z_1\left(\frac{N^*}{2}\right)$$

$$\Rightarrow \boxed{Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 u_{Avg}(N^*)^2}$$

(# collisions per unit time unit vol.)

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

$$\Rightarrow \frac{N}{V} = \frac{PN_A}{RT} \Rightarrow N^* \propto \frac{P}{T}$$

$$\Rightarrow Z_{11} \propto \sqrt{T}\left(\frac{P}{T}\right)^2 \Rightarrow Z_{11} \propto \frac{P^2}{T^{3/2}}$$

For const. P, $\boxed{Z_{11} \propto \frac{1}{T^{3/2}}}$

For const. T, $\boxed{Z_{11} \propto P^2}$

For const. V, (Closed Container) $\boxed{Z_{11} \propto \frac{1}{T^{1/2}}}$

Mean Free Path : Avg. dist. travelled by a gas particle b/w 2 successive collisions

$$\left(\begin{array}{c}\text{Mean Free Path}\\ \text{Length}\end{array}\right) = \left(\frac{\text{Total dist. travel in 1s}}{\text{\# Collisions in 1s by 1 particle}}\right)$$

$\Rightarrow \quad \lambda = \left(\frac{u_{Avg}}{Z_1}\right) \Rightarrow \boxed{\lambda = \left(\frac{1}{\sqrt{2}\,\pi\sigma^2 N^*}\right)}$

Now, $N^* \propto \frac{P}{T} \Rightarrow \lambda \propto \frac{T}{P}$

for const. P, $\lambda \propto T$

for const. T, $\lambda \propto 1/P$

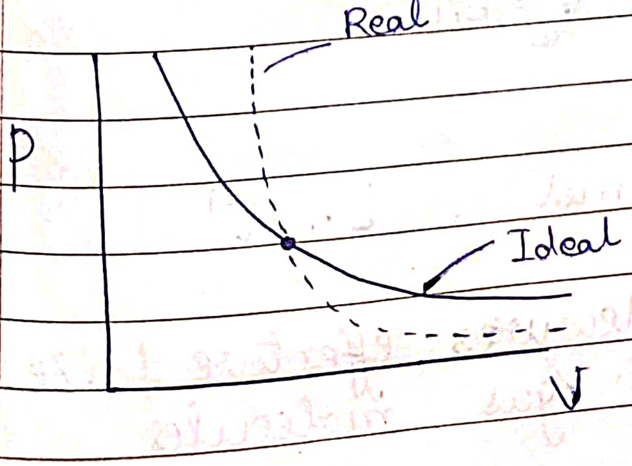
for const. V, (Closed Container) $\lambda = \text{Const.}$

Real Gas

- Real gases do NOT follow ideal gas laws, at all temp. & prsre.

- They show significant deviation from ideal behavior at high pressure.

- They may behave as ideal gas at low prsre & high temp.



At high P, $V_{real} > V_{Ideal}$

At Low P, $V_{real} < V_{ideal}$

Cause of Deviation :

- Vol. of gas particles is NOT negligible wrt container.

- There EXIST intermolecular forces among gas particles.

Real Gas Eq^n (Van der Wall's Eq^n) –

The eq^n is derived by considering vol. occupied by gas molecules, as well as attractive forces.
(rep. forces NOT considered)

Vol. Correction : $V_{free\ mot.} = V_{ideal}$ (by def^n)

$$\Rightarrow \quad V_{ideal} = V_{real} - \underbrace{v}_{\text{vol. correction}}$$

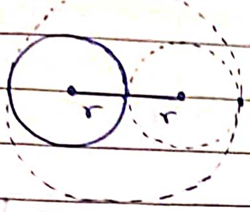
Now, $v \propto n \Rightarrow v = bn$

$$\Rightarrow \quad V_{ideal} = V_{real} - bn$$

Units of $b = m^3 mol^{-1}$, $L mol^{-1}$

Significance of b ⇒ Measures effective size of gas molecules.

Calculation of b:



For pair of molecules,

$$\begin{pmatrix}\text{Excluded}\\ \text{Vol.}\end{pmatrix} = \frac{4}{3}\pi(2r)^3$$

For a single molecule,

$$\begin{pmatrix}\text{Excluded}\\ \text{Vol.}\end{pmatrix} = \frac{2}{3}\pi(2r)^3$$

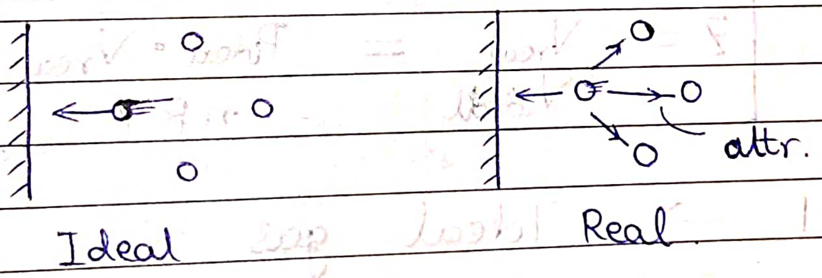
For 1mol molecule,

$$\begin{pmatrix}\text{Excluded}\\ \text{Vol.}\end{pmatrix} = N_A\cdot\frac{2}{3}\pi(2r)^3 = 4\cdot\left(\frac{N_A\cdot 4\pi r^3}{3}\right)$$

$$\Rightarrow \boxed{b = 4\begin{pmatrix}\text{Vol. of 1mol}\\ \text{gas particles}\end{pmatrix}}$$

Pressure Correction: $P_{real} = P_{ided} - p$

prsre correction



'p' depends on : 1) force of collision 2) freq. of collision

both of which depend on force of altr.

Now, force of altr. $\propto \left(\frac{n}{V}\right)$ {no. of moles per vol.}

$$\Rightarrow p \propto \left(\frac{n}{V}\right)^2 \Rightarrow \boxed{p = \frac{an^2}{V^2}}$$

326 $P_{ideal} = P_{real} + \left(\frac{an^2}{V^2}\right)$

'a' measure of force of attr. b/w gas molecules

Units of a = $atm\,L^2\,mol^{-2}$

Final eq^n –

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

Compressibility Factor (Z) –

Measure of extent of deviation of real gas from ideal behavior.

$$\boxed{Z = \frac{V_{real}}{V_{ideal}} = \frac{P_{ideal} \cdot V_{real}}{nRT}}$$

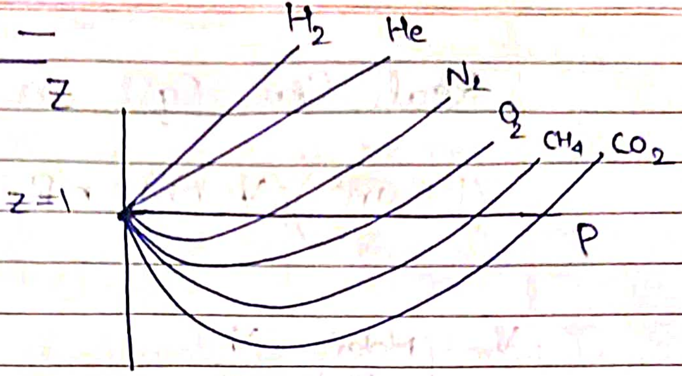
- $Z = 1 \Rightarrow$ Ideal gas.
- $Z \neq 1 \Rightarrow$ Real gas

$Z < 1$
- $V_r < V_i$
- Low gas P.
- (–ve) deviation
- Attr forces dominant
- Compressible

$Z > 1$
- $V_r > V_i$
- High gas P
- (+ve) deviation
- Rep. forces dominate
- Incompressible

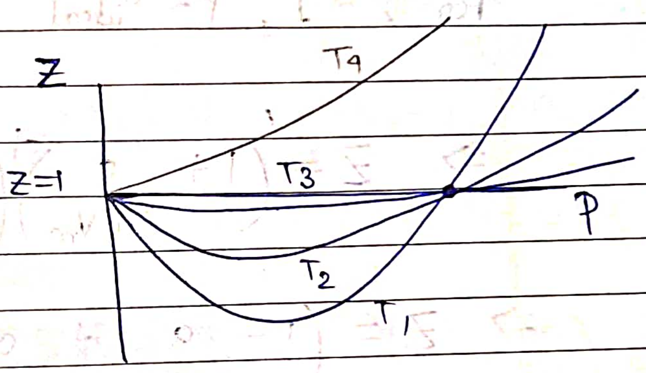
Variation of Z vs P –

At same temp.



Variation of Z vs P (for a specific gas) –

$T_4 > T_3 \overset{>}{\bullet} T_2 \overset{>}{\bullet} T_1$



Boyle Temp.:
Temp. at which gas shows ideal behavior over good amt. of P values.

$$\boxed{T_b = \frac{a}{Rb}}$$

Now, for 1 mol gas $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

- Low P, Moderate T : $\left(P + \frac{a}{V^2}\right)V = RT \Rightarrow \boxed{Z = 1 - \frac{a}{VRT}}$
  $\Rightarrow$ V high
- Low P, High T : $\boxed{PV = nRT}$
  $\Rightarrow$ V very high
- High P $\Rightarrow$ V low : $P(V-b) = RT \Rightarrow \boxed{Z = 1 + \frac{Pb}{RT}}$

Real Gas Eq^n in Virial State –

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT \Rightarrow \left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

$$V_m=\left(\frac{\text{Molar}}{\text{vol.}}\right)=\frac{V}{n} \qquad \Rightarrow PV_m\left(1+\frac{a}{PV_m^2}\right)\left(1-\frac{b}{V_m}\right)=RT$$

$$\text{for } Z\approx 1,\ P\approx P_{ideal} \qquad \Rightarrow \left(\frac{P_{ideal}V_m}{RT}\right)=\left(1+\frac{a}{P_{ideal}V_m^2}\right)^{-1}\left(1-\frac{b}{V_m}\right)^{-1}$$

$$\Rightarrow Z=\left(1+\frac{a}{RTV_m}\right)^{-1}\left(1-\frac{b}{V_m}\right)^{-1} \quad \Big\downarrow \left\{\begin{matrix}\text{Binomial}\\\text{Theorem}\end{matrix}\right\}$$

$$\Rightarrow Z=\left(1-\frac{a}{RTV_m}+\frac{a^2}{R^2T^2V_m^2}\right)\left(1+\frac{b}{V_m}+\frac{b^2}{V_m^2}\right)$$

$$\Rightarrow Z=1+\left(\frac{1}{V_m}\right)\underbrace{\left(b-\frac{a}{RT}\right)}_{\text{2nd virial coeff.}}+\left(\frac{1}{V_m^2}\right)\underbrace{(b^2)}_{\text{3rd virial coeff.}}$$

$$\text{for } Z=1, \qquad \boxed{T=\left(\frac{a}{Rb}\right)} \text{ – Boyle's Temp.}$$

Critical Temp., Prsre, Vol. –

(T_c) Critical Temp: Highest temp. at which liquid state can be obtained.

(V_c) Critical Vol: Vol. of 1 mol of gas at T_c

(P_c) Critical Prsre: Prsre of 1 mol of gas at T_c.
(Min. prsre for liq. of gas at T_c)

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

$$\Rightarrow (V_m-V_1)(V_m-V_2)(V_m-V_3)=0$$

When $V_1 = V_2 = V_3 = V_c$,

$$\Rightarrow 3V_c = \left(b+\frac{RT_c}{P_c}\right), \quad 3V_c^2 = \left(\frac{a}{P_c}\right), \quad V_c^3 = \left(\frac{ab}{P_c}\right)$$

$$\Rightarrow \boxed{V_c = 3b}, \quad \boxed{P_c = \left(\frac{a}{27b^2}\right)}, \quad \boxed{T_c = \left(\frac{8a}{27bR}\right)}$$

$$* \quad Z_c = \frac{P_cV_c}{RT_c} \Rightarrow \boxed{Z_c = \frac{3}{8}}$$

Law of Corresponding States –

(Reduced P, V, T)

Let $P_r = \frac{P}{P_c}$, $T_r = \frac{T}{T_c}$, $V_r = \frac{V}{V_c}$

$$\Rightarrow \boxed{\left(P_r+\frac{3}{V_r^2}\right)(3V_r-1) = 8T_r} \quad \text{&} \quad \boxed{Z = \frac{3}{8}\frac{P_rV_r}{T_r}}$$

Eudiometry

Absorbant	Gas absorbed
NaOH or KOH	Acidic gases, CO_2, SO_2, NO_2
Ammonical Cu_2Cl_2	CO, C_2H_2
Turpentile oil	O_3
Alkaline Pyrogallol	O_2
Conc. H_2SO_4	Moisture, NH_3
$FeSO_4$ sol^n	NO
Heated Mg	N_2

* Ignore vol. of liquids in calc., in most cases, unless not negligible.

Q) (Exercise 4, Q4, Gaseous State Module)

A) Reactants: CH_4, C_2H_4 (CO_2 doesn't react)

Vols: $CH_4 \rightarrow V_1$, $C_2H_4 \rightarrow V_2$, $\underset{\text{init.}}{CO_2} \rightarrow V_3$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$V_1 \text{ mL} \quad 2V_1 \text{ mL} \quad V_1 \text{ mL}$$

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

$$V_2 \text{ mL} \quad 3V_2 \text{ mL} \quad 2V_2 \text{ mL}$$

$$\text{Contraction } 1 = 17 = -(2V_2 + V_1 + V_3) + (3V_1 + 4V_2 + V_3)$$

$$\Rightarrow \boxed{17 = 2V_1 + 2V_2}$$

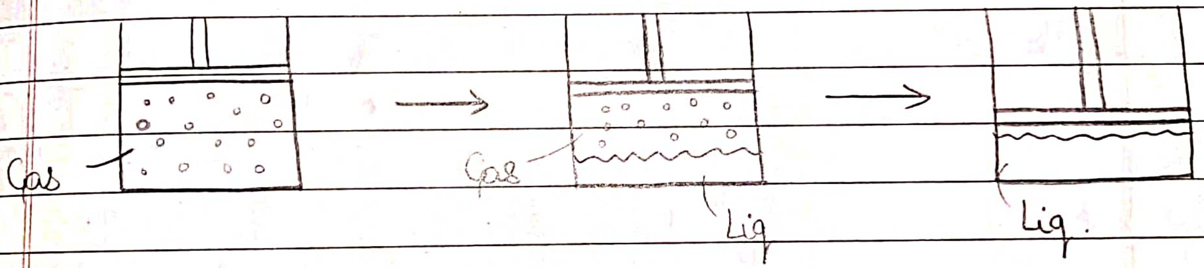
KOH absorbs CO_2 ⇒ $\underbrace{V_1}_{(I)} + \underbrace{2V_2}_{(II)} + \underbrace{(10-V_1-V_2)}_{\text{initial}} = 14$

⇒ $\boxed{V_2 = 4}$

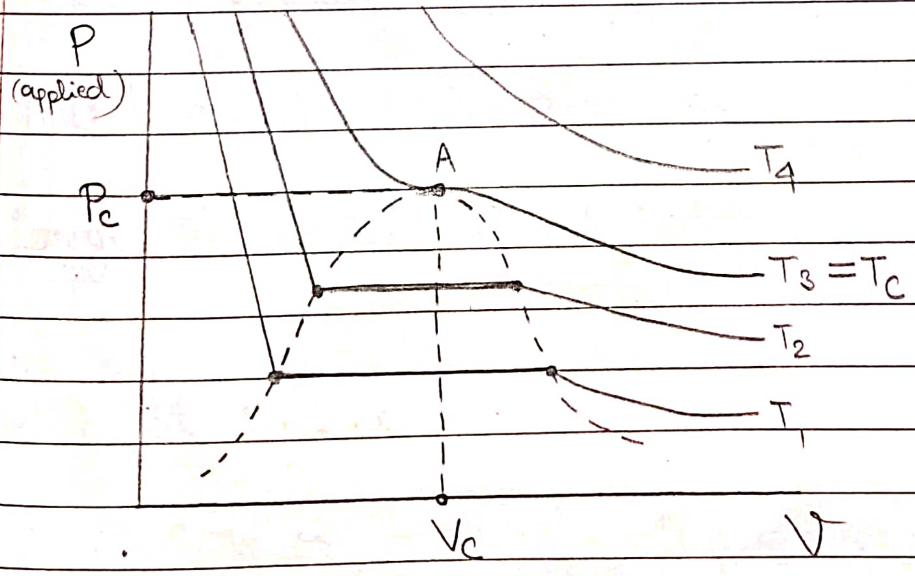
⇒ $\boxed{V_1 = 4.5}$ ⇒ $\boxed{V_3 = 1.5}$

● $\boxed{4.5\text{ mL } CH_4,\quad 4\text{ mL } C_2H_4,\quad 1.5\text{ mL } CO_2}$

Andrew's Isotherm



Plotted at a const. temp.



At A, $\rho_{liq} = \rho_{gas}$