

Boyle's Law

At $T = \text{const}$

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

$$P_1 V_1 = P_2 V_2$$

Pressure = 1 atm

= 760 mm of Hg

= 76 cm of Hg

= 1 bar

= 760 torr

= 14.7 psi

= $10^5 \text{ Pa (N/m}^2\text{)}$

Volume

1 L = 1000 mL or cc

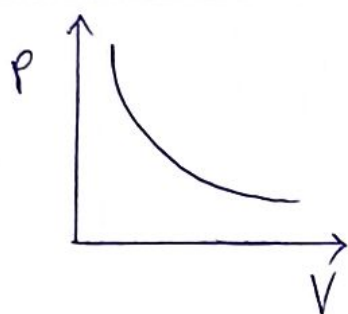
= $\frac{1}{1000} \text{ m}^3$

= 1 dm^3

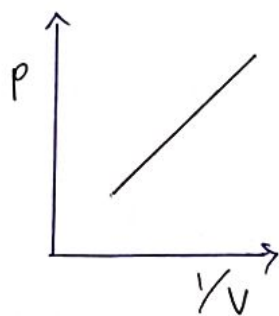
= 1000 cm^3

GRAPHS

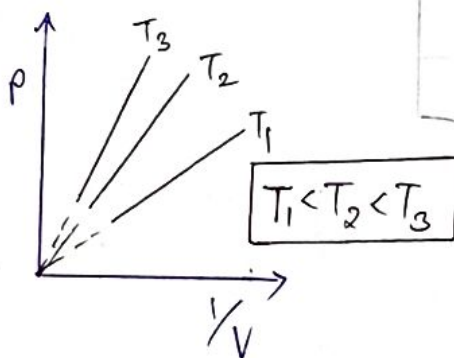
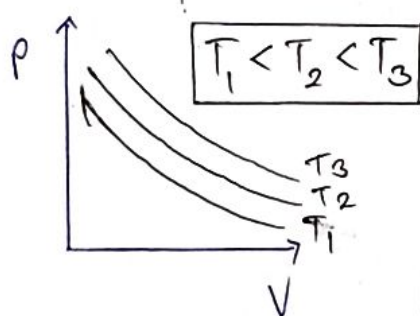
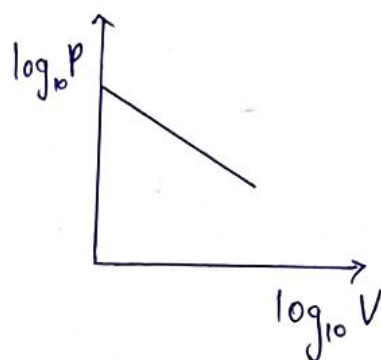
① P vs V



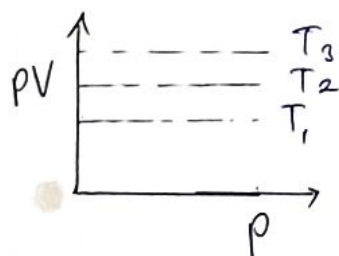
② P vs $1/V$



③ $\log_{10} P$ vs $\log_{10} V$

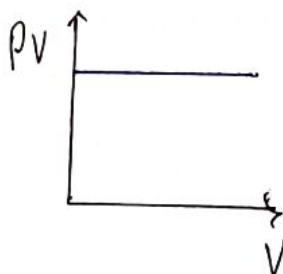


④ PV vs P



$$T_1 < T_2 < T_3$$

⑤ PV vs V



Charles's Law

At $P = \text{constant}$

$$V \propto T$$

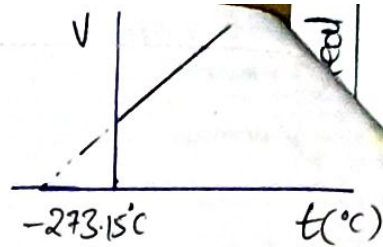
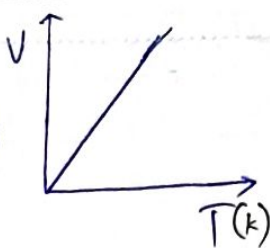
$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

• If V_0 is the volume of a given mass of gas at 0°C & V_t is its volume at any temperature $t^\circ\text{C}$, then

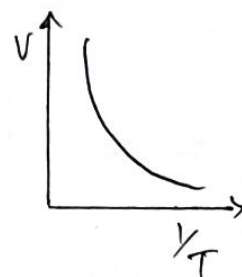
$$V_t = V_0 \left[1 + \frac{t}{273} \right]$$

Graphs

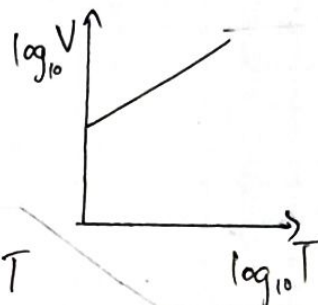
① V vs $T(K)$



② V vs $1/T$



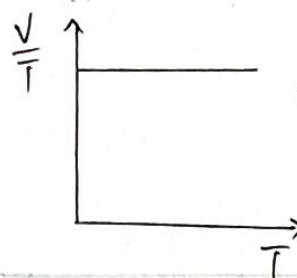
③ $\log_{10} V$ vs $\log_{10} T$



④ V/T vs V



⑤ V/T vs T



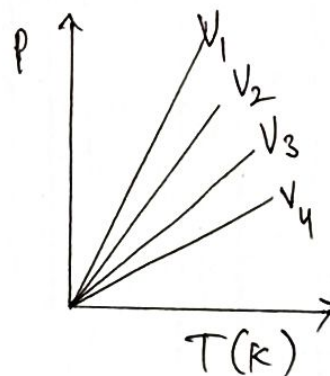
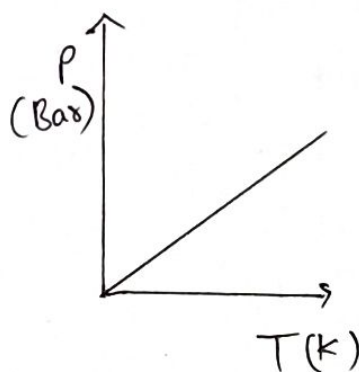
Gay-Lussac's Law

At $V = \text{constant}$,

$$P \propto T$$

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

• A graph plotted Btwn P & T at constant V is called isochore.



$$V_1 < V_2 < V_3 < V_4$$

Avogadro's Law

constant = T & P

→ Graphs same as Charles law.

$$V \propto n$$

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

Ideal Gas Equation

A, B, C

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

$$PV = nRT$$

R = Universal gas C.

$$= 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \left(\frac{25}{3} \right)$$

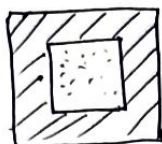
$$= 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \left(\frac{1}{12} \right)$$

$$= 1.98 \frac{\text{cal}}{\text{mol} \cdot \text{K}} (2)$$

Types of containers

I) Closed containers:

i) Rigid closed containers



$V = \text{fixed}$
(Const.)
 $n = \text{const.}$

$$\therefore P \propto T$$

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

ii. Movable closed containers



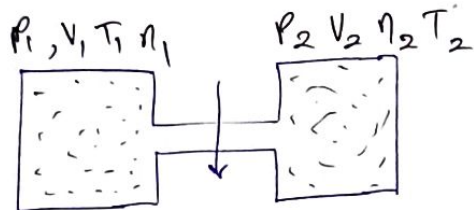
$n = \text{const.}$

$$PV = nRT$$

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

Eg. Bubble, Ballon
Air

II) Connected containers



$$\Rightarrow n_1 + n_2 = n_f$$

$$\Rightarrow V_1 + V_2 = V_f$$

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

$$\frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2} = \frac{P_f V_f}{T_f}$$

Open containers:



$P = \text{same}$

$V = \text{same}$

$n, T \rightarrow \text{vary.}$

$$PV = nRT$$

$$nT = \text{const}$$

$$n_1 T_1 = n_2 T_2$$

Combined gas Law

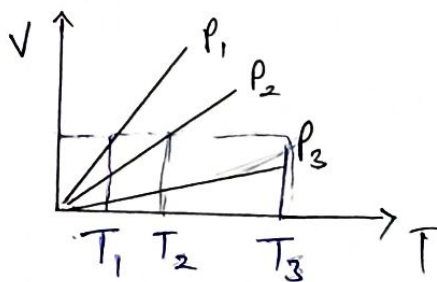
for a fixed amount of gas,
if temp, pressure & volume
changes from $T_1, P_1, V_1 \rightarrow T_2, P_2, V_2$

$n = \text{constant } (n_1 = n_2)$

$$PV = nRT$$

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

Compare pressure?



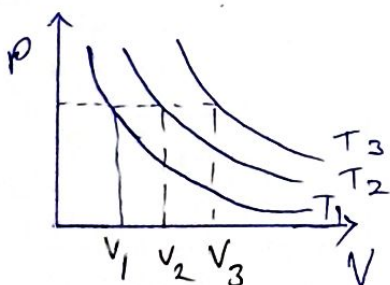
$$T_1 < T_2 < T_3$$

$$V \propto \text{const}$$

$$P \propto T$$

$$\therefore P_1 < P_2 < P_3$$

Compare Temperature



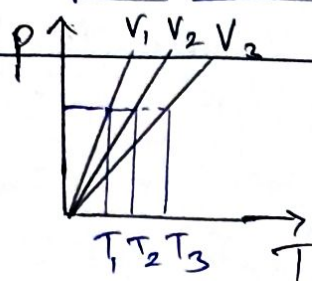
$$V_1 < V_2 < V_3$$

$$\therefore P = \text{const}$$

$$\therefore (V \propto T)$$

$$\therefore T_1 < T_2 < T_3$$

Compare Volumes?



$$T_1 < T_2 < T_3$$

$$P = \text{const}$$

$$\therefore V \propto T$$

$$V_1 < V_2 < V_3$$

Dalton's Law of Partial Pressure

For non-reacting gaseous mixture the total pressure exerted is the sum of partial pressure (Individual pressure) of each gas.

$$P_T = P_1 + P_2 + P_3 + \dots$$

(at Const. V & T)

$$P_{\text{gas}} = X_{\text{gas}} P_T$$

P_{gas} = Partial pressure of gas

$$\% \text{ of gas in a mixture} = \frac{\text{Partial Pressure of a gas (P)}}{P_{\text{Total}}} \times 100$$

$$\text{fraction of total pressure} \left(\frac{P_{\text{gas}}}{P_{\text{Total}}} \right) = X_{\text{gas}}$$

Vapour Pressure :- The pressure exerted by vapours over the surface of liquid when liquid & vap. are in equilibrium.

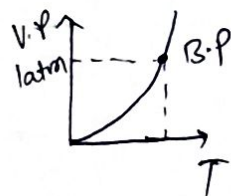


Factor affecting V.P.:

① Temp

$$T \uparrow \Rightarrow V \uparrow \Rightarrow V.P \uparrow$$

$$V.P \propto T$$



② Intermolecular force:

$$V.P \propto \frac{1}{\text{I.M.F of liq}}$$

• Pressure exerted by saturated water vapour is called aqueous tension

$$P_{\text{dry gas}} = P_{\text{total}} - \text{aqueous } T$$

or
Moist gas

Diffusion :- The spon. flow of gas molecules from higher concⁿ to lower concⁿ is called diffusion.

Effusion :- forced diffusion is called effusion.

The spon. flow of ^{OR} gas molecules from higher concⁿ to lower concⁿ via small hole (or pin hole or orifice)

Graham's Law : The rate of diffusion or Effusion is inversely prop. to the square root of the density of the gas at (const. P & T)

$$\therefore r \propto \frac{1}{\sqrt{d}} \quad \left[\text{Rate of diffusion } (r) = \frac{\text{Volume of gas diffused}}{\text{time taken } (t)} \right]$$

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} = \frac{t_2}{t_1}$$

d = density of gas.
 M = Molecular masses

- Volume flow rate
- Moles flow rate
- Length flow rate

$$r = \frac{V}{t}$$

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

$$r = \frac{n}{t}$$

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

$$r = \frac{l}{t}$$

$$\frac{l_1}{l_2} \times \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

If P is variable : $r \propto \frac{1}{\sqrt{M}}$; $r \propto P$

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

Kinetic gas Equation :

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

P : Pressure (Pa or N/m^2)

V → Volume (m^3)

m → mass of molecule (kg)

N → No. of molecules

v_{rms} = Root mean square velocity. (m/s)

Relative B/w avg. k.E & absolute Temp (T)

$$PV = \frac{1}{3} m N V_{rms}^2 = \frac{2}{3} \times \left(\frac{1}{2} m N V_{rms}^2 \right) \Rightarrow \boxed{\frac{3nRT}{2} = \text{Avg k.E}}$$

for n moles, $\text{Avg k.E} = \frac{3}{2} nRT$

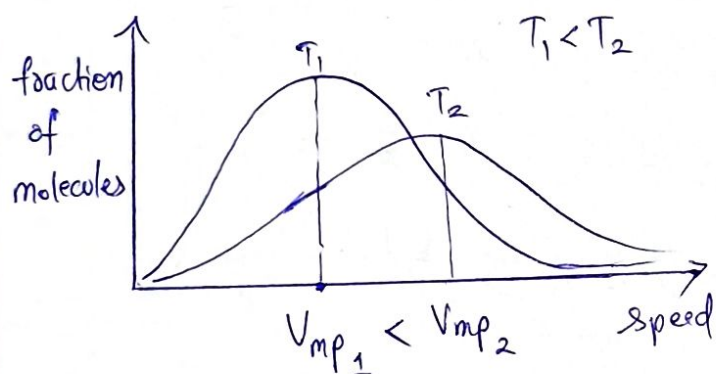
for 1 mole, $\text{Avg k.E} = \frac{3}{2} RT$

for 1 molecule $\text{Avg k.E} = \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} k_B T \quad \left(\frac{R}{N_A} = k_B \right)$

$$k_B = 1.380 \times 10^{-23}$$

• The distribution of velocity can be calculated by probability and it may be concluded as (unsymmetrical graph)

1. Small fraction of molecules have very low & very high velocities.
2. Curve become flat on increasing temp.
3. Most of the molecules have most probable velocity.



fraction of Molecules $f(v) =$

$$4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

$$[V_{mp} \propto T]$$

Most Probable (V_{mp}):

$$f'(v) = 0$$

$$V_{mp} = \sqrt{\frac{2kT}{m}}$$

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

k = Boltzman constant

T = Temperature

m = mass of gas molecule (kg)

M = Molar mass

$$R = 8.314 \text{ or } \left(\frac{25}{3} \right)$$

$$\boxed{k = \frac{R}{N_A}}$$

Avg. Velocity :

$$V_{avg} = \frac{n_1 c_1 + n_2 c_2 + n_3 c_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

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

$$V_{avg} = \sqrt{\frac{8kT}{\pi m}}$$

R.M.S velocity :

$$V_{rms} = \sqrt{\frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \dots}{n_1 + n_2 + n_3}}$$

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

$$V_{rms} = \sqrt{\frac{3kT}{m}}$$

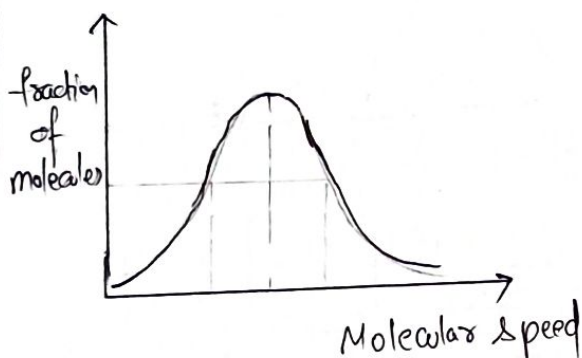
$$R > A > M$$

Ratio:

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

$$\Rightarrow V_{rms} > V_{avg} > V_{mp}$$

* If Maxwell - Boltzmann Curve is symmetrical then :



$$V_{rms} > V_{avg} = V_{mp}$$

→ Mean free path, Collision freq. & Mean free time

① KTG is valid

• Only one molecule is moving

• Mean free path (λ)

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

σ = Collision diameter

N^* = Number density = $\frac{N}{V}$
(No. of molecule per unit volume)

$$PV = nRT$$

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

$$\frac{N}{V} = \frac{PN_A}{RT} \quad \text{--- (1)}$$

$$N^* = \frac{PN_A}{RT} = \frac{P}{kT}$$

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

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

Mean free time

$$\tau = \frac{1}{Z} = \frac{1}{\sqrt{2} \pi \sigma^2 V_{avg} N^*}$$

$$\lambda = \frac{V_{avg}}{\tau}$$

Collision freq (Z): No. of collision per second per unit

$$Z = \frac{1}{\sqrt{2} \pi \sigma^2 V_{avg} N^*}$$

Real gas

* Two postulates of KTG do not hold good.

1. There is no force of attraction b/w gas molecules
2. Molecular volume is negligible.

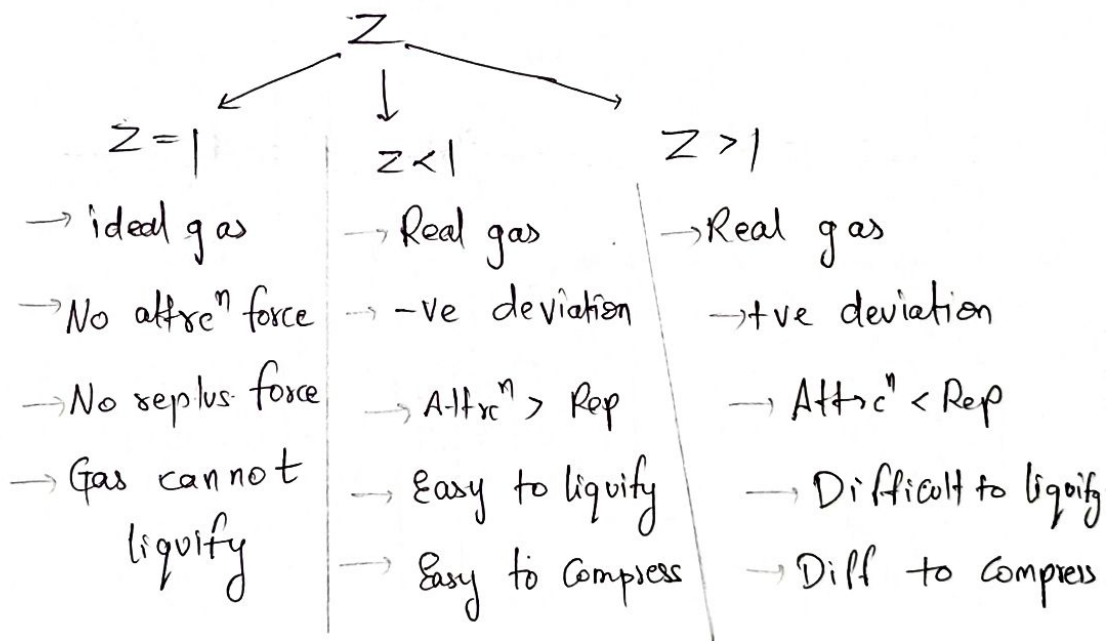
① Compressibility factor (Z)

$$Z = \frac{PV_{obs}}{nRT}$$

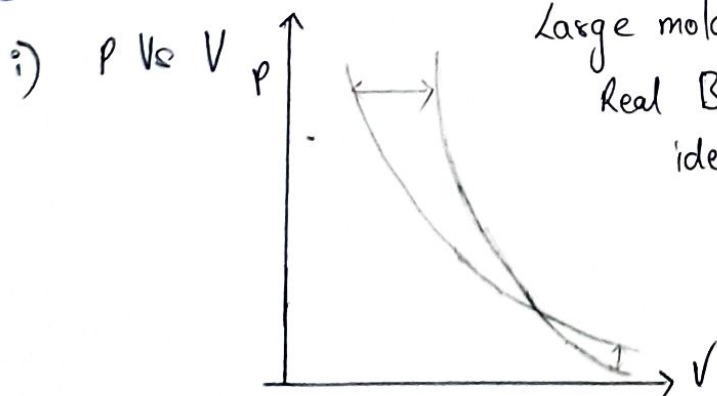
$$Z = \frac{V_{obs}}{\frac{nRT}{P}}$$

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

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

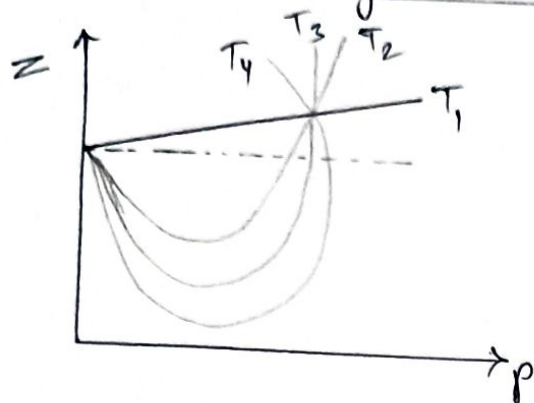


② Graphical analysis



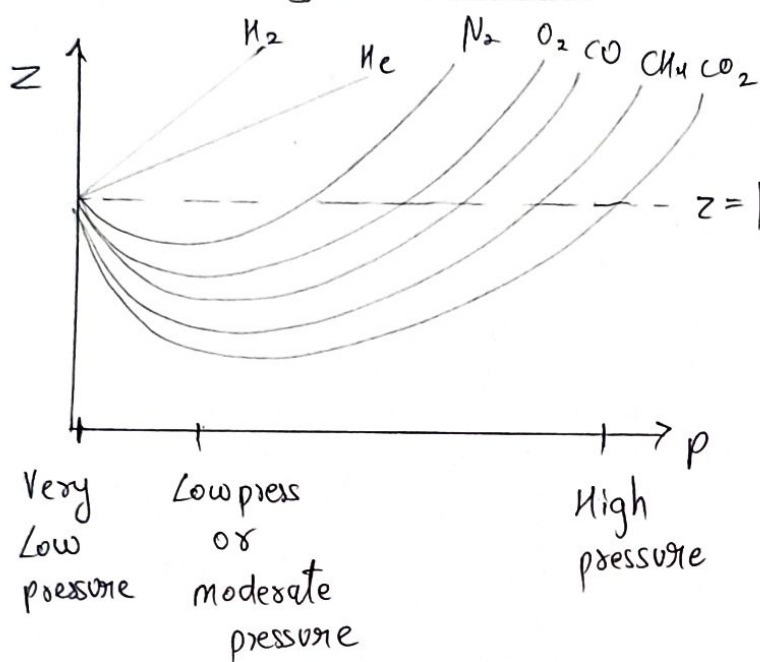
Large molar volume per
Real Behaves like
ideal.

② Z vs P for a gas at different temp.



$$T_1 > T_2 > T_3 > T_4$$

③ for different gases at same Temperature



Case 1: At very low pressure
 $Z = 1$ (All gases)

Case 2: At low pressure
 $Z < 1$ (Except H_2 & He)

Case 3: At high pressure
 $Z > 1$ (All gases)

Case 4: for H_2 & He

①

$$Z = 1$$

At very
Low pressure

②

$$Z > 1$$

At Low (moderate)
& High pressure

③ Vander Waal Equation

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

Pressure correction
term

$$\left(+\frac{n^2 a}{V^2}\right)$$

Volume Correction
term

$$(-nb)$$

① $a, b \rightarrow$ depends on Nature of the
gas
Independent of the temperature

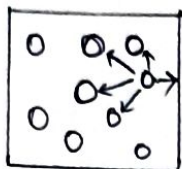
② $a, b \rightarrow$ vander waal constant

a - measure of intermolecular attrcⁿ force & connected with liquefaction
 b - Excluded Volume or Co-volume.

① Pressure correction term



ideal



Real

$$P_{\text{ideal}} > P_{\text{real}}$$

$$P_i = P_r + \frac{n^2 a}{V^2}$$

$$PCT \propto \frac{n}{V} \times \frac{n}{V}$$

$$PCT \propto \frac{n^2}{V^2}$$

$$PCT = \frac{n^2 a}{V^2}$$

② Volume correction term

ideal

Real

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

Bimolecular collision



$$\text{Volume excluded for 2 molecules} = \frac{4}{3} \pi (2r)^3$$

$$\text{Volume excluded for 1 molecule} = \frac{2}{3} \pi (2r)^3$$

$$\text{Volume for } N_A \text{ molecules} = \frac{16}{3} \pi r^3 N_A$$

$$b = 4 V_m N_A = 4 V_m$$

$$P_i V_i = nRT$$

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

Case I: At very low pressure ($z=1$)

$a = \text{neglected}$, $b = \text{neglected}$

$$\therefore PV = nRT$$

$$\therefore z = 1$$

2: At low pressure or moderate ($z < 1$)

$b = \text{neglected}$

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

$$(pV + \frac{n^2 a}{V}) = nRT$$

for 1 mole,

$$\left(pV_m + \frac{a}{V_m}\right) = RT$$

$$\frac{pV_m}{RT} + \frac{a}{RTV_m} = 1$$

$$Z + \frac{a}{RTV_m} = 1$$

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

$$\therefore Z < 1$$

Case 3: At high pressure ($z > 1$)

$a = \text{neglected}$

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

$$p(V - nb) = nRT$$

for 1 mole

$$pV_m - pb = RT$$

$$\frac{pV_m}{RT} - \frac{pb}{RT} = 1$$

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

$$\therefore Z > 1$$

Case 4: for H_2 & He

$$z = 1$$

$$z > 1$$

$$z = 1 + \frac{pb}{RT}$$

* OMG

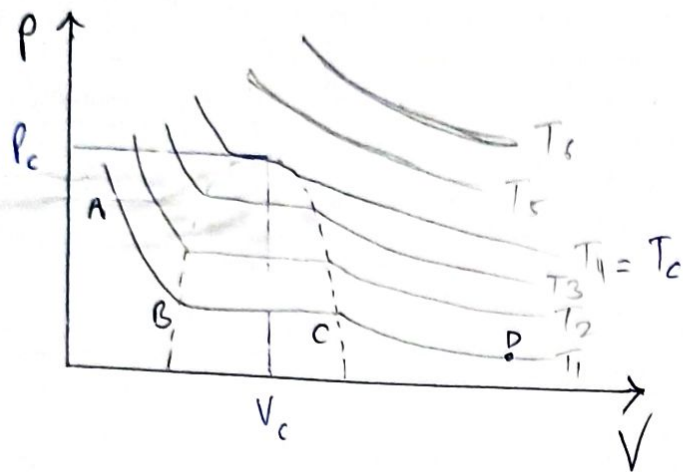
① At low pressure and High temp.

Ideal = Real.

② At high pressure & Low temp \rightarrow
Maximum deviation

Liquefaction of gases

Andrew CO_2 isotherm



$AB \rightarrow \text{liquid}$

$BC \rightarrow \text{liquid} \rightleftharpoons \text{Vap}$

$CD \rightarrow \text{gas}$

$$T_1 < T_2 < T_3 < T_4 < T_5 < T_6$$

- Critical Temperature (T_c) : The Temp. above which gas cannot be liquify.

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

- Critical Pressure (P_c) : The pressure at T_c is called P_c

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

- Critical Volume (V_c) : The volume of 1 mol of the gas at P_c, T_c is called V_c

$$V_c = 3b$$

★ OMT : $\frac{dP}{dV} = 0$ & $\frac{d^2P}{dV^2} = 0$ at Critical point.

Compressibility factor at c.P (Z_c) :

$$Z_c = \frac{P_c V_c}{nRT_c} = \frac{\frac{a}{27b^2} \times 3b}{nR \left(\frac{8a}{27Rb} \right)} = \frac{3}{8} < 1$$

andⁿ for liquifaction

$a \uparrow$ liquefaction \uparrow

b ↓ liquefaction ↓

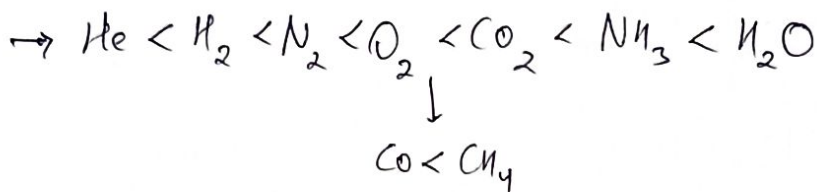
$$T_c = \frac{2a}{27Rb}$$

$$T_c \propto \frac{a}{b}$$

liquefaction $\propto \frac{a}{b}$

liquefaction $\propto \frac{a}{b}$

- Liq & Tc



Boyle's Temp

The Temp when Real gas Behaves like ideal

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

Compare T_i, T_B & T_c

$$T_i = \frac{2a}{Rb}$$

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

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

$$T_i > T_B > T_c$$

Temperature :

$$^{\circ}\text{F} = \frac{9}{5}^{\circ}\text{C} + 32$$

$$T(\text{K}) = t^{\circ}\text{C} + 273.15$$

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

$$\Rightarrow C_{\text{MP}} : C_{\text{avg}} : C_{\text{rms}} = 1 : \underline{1.128} : \underline{1.224}$$

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

$$\text{Units of } a = \text{L}^2 \text{mol}^{-2} \quad \& \quad b = \text{L mol}^{-1}$$

$$\Rightarrow \text{Density of water vapour at Boiling point of water is } \underline{6 \times 10^{-4} \text{ g/cm}^3}$$

$$\Rightarrow \Delta H_{\text{vap}} = \frac{2.303 R T_1 T_2}{(T_2 - T_1)} \log\left(\frac{P_2}{P_1}\right)$$

$$\Rightarrow \text{for isothermal reaction of ideal gas enthalpy change is } \underline{\text{ZERO}}$$