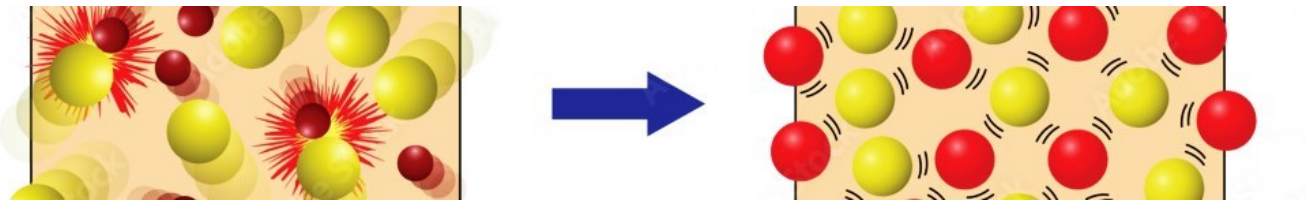
Summary Notes on

CH 1201

Gas Laws, KTG and Liquid State



Spring 2023

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GAS LAWS



4/5/2023
PP

1. Ideal Gas Eqn: $PV = nRT$. 1.E.1

1.1 Gas Laws (ideal)

Boyle's Law $V \propto \frac{1}{P}$ (n, T) fix.

Charles' Law $V \propto T$ (n, P) fix.

Avogadro's Law $V \propto n$

* At Low P, High T, Real gas ⟶ Ideal gas. (perfect).

1.2 Universal Gas Constant (R)

At STP, one mole gas, occupies 22.4 L

IUPAC : STP: $T = 273.15\,K$, $P = 1\,bar = 0.987\,atm$.

NIST : NTP: $T = 293.15\,K$, $P = 1\,atm$

$$R = \frac{PV}{nT} = 0.082 \left(\frac{L \cdot atm}{mol \cdot K}\right)$$

$1\,J = 10^7\,erg$ $= 8.314 \frac{J}{mol \cdot K}$.

$R \simeq 2 \frac{cal}{mol \cdot K}$

Boltzmann constant.

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \frac{m^2 \cdot kg}{s^2 \cdot K}.$$

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1.3 Other forms of ideal gas eqn.

1.3.1

$$PV = \frac{W}{M} RT$$

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

1 torr = 1 mm of Hg

1 atm = 760 torr.

1 bar = 10^5 Pa = 750 torr.

1 Pa = 10 dyne cm^{-2}.

1.3.2

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

$$P = N' K_B T$$

N' = Number Density

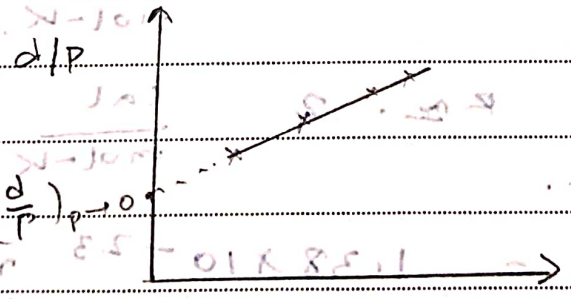
$= N/V$

1.4 Limiting Density.

- Not valid for Real gases at all.

$$M = \left(\frac{d}{P}\right)_{P \to 0} RT$$

$\left(\frac{d}{P}\right)_{P \to 0}$ = Limiting density of gas at temp T



1.5 Vapour Density

Who undergo dissociation
substitute do not show density
ab novidade vapi density
① $2HI \rightleftharpoons H_2 + I_2$

V.D = density of gaseous state of substance.

Density of H_2 / Under same T & PV

② Measurement of density at constant volume

Expected V.D, $D_0 = \frac{M_0}{2}$. | α = Degree of Dissociation

	AB →	xA +	yB
t=0	n	0	0
	$n(1-\alpha)$	$x\alpha$	$y\alpha$

$V_{after\ dissio} = V_0(1 + (n-1)\alpha)$ ← initial; ↓ no. of particles dissociate

$V\alpha \frac{1}{M}$

Initial moles, $n = \frac{W}{M}$.

$n_{total} = n(1-\alpha) + x\alpha + y\alpha$.

$\therefore PV = (n_{total})RT$

% of B by wt. = $100 \times \alpha$

% of B by vol = $\frac{y\alpha}{n_{total}} \times 100$.

1.6 Partial Pressure. (Dalton)

$P = P_a + P_b + P_c + \dots$

where $P_i = \frac{n_i RT}{V}$

$\therefore P = \sum P_i = (\sum n_i)\frac{RT}{V} = \frac{NRT}{V}$

$\Rightarrow P_i = P x_i$ $\quad x_i = \frac{n_i}{N}$ (mole fraction).

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1.7 Partial volume (Amagat)

$$V = \sum v_i$$

$$v_i = \frac{n_i RT}{P}$$

$$v_i = x_i V$$

1.8 Coefficients

1.8.1 Coeff. of Thermal Expansion (α)

$$\alpha = \frac{w}{M} \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

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

$$\therefore \alpha = \frac{1}{V}\left(\frac{R}{P}\right) = \frac{1}{T}$$

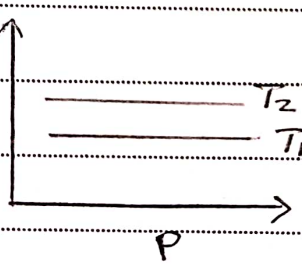
Doesn't depend on nature of gas.

1.8.2 Coeff of compressibility (β)

$$\beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{-RT}{P^2} \quad \therefore \beta = \frac{1}{P}$$

1.9 PV v/s P



1.10) Ideal gas has no intermol- aHr, Hence cannot be liquified.

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2. Real Gas

2.1 Coefficients

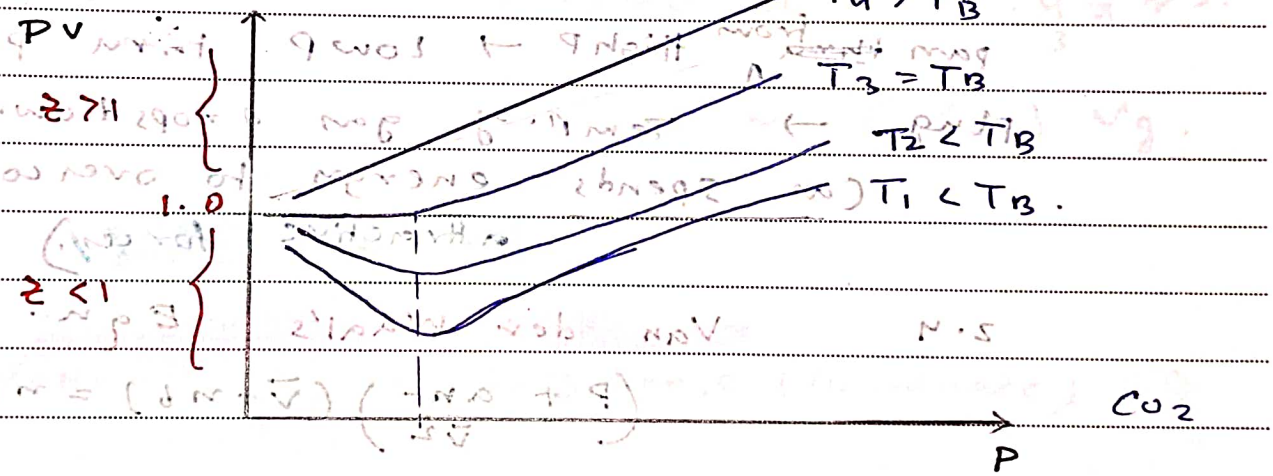
Both α and β depend on nature of gas.

2.2 Compressibility factor (Z)

Measure of extent of deviation of the real gas.

$$Z = \frac{PV}{RT} = \frac{V_{obs}}{V_{id}} = \frac{P_{obs}}{P_{id}}$$

Amagat curve



% deviation $= \frac{|P - P_{id}|}{P_{id}} \times 100 = \frac{|V - V_{id}|}{V_{id}} \times 100$

2.2.1 Analysis of PV v/s P graph.

2.2.2.

- $T < T_B$ — $b - \frac{a}{RT}$ — (+ve) Intermol. Attr. Dominate
- $T = T_B$ — $Z = 1$
- $T > T_B$ — $b - \frac{a}{RT}$ — (+ve) Size Effect Dominate.

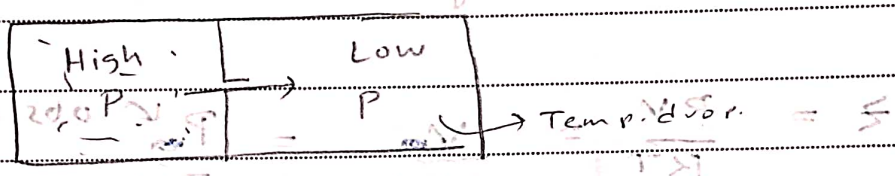
(A) $Z < 1$

Gas exert lower Pr. → Higher Intermol. Forces → More compressible than ideal gas.

(B) $Z > 1$

Gas exert higher Pr. → vol. of gas higher (than ideal gas) → Gas become less compressible.

2.3 Joule Thomson Effect.



2 comp. at same Temp; if Real gas pass from High P → Low P thru porous plug → Temp. of gas drops down. (Gas spends energy to overcome attractive forces)

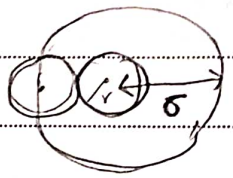
2.4 Van der Waal's Eqn.

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

2.4.1. Covolume (b)

σ = Dist. of closest approach, = collision diameter

$r = \sigma/2$ = Van der Waal Radius,



2 → $4/3\pi\sigma^3$ (Excluded vol.)

1 → $2/3\pi\sigma^3$

1 mole → DOMS $b = \frac{2}{3}\pi N_A \sigma^3$

$P_{id}(\bar{V} - nb) = nRT$

∴ n mole → nb

$= n\left(\frac{2}{3}\pi N_A (8r^3)\right)$

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

$= n \times 4 \times$ (Actual vol. of 1 mole of gas)

$\bar{V} = V_{actual} = \bar{V}_{id} + nb \Rightarrow V_{id} = \bar{V} - nb$.

$b \rightarrow$ Measure of Repulsive forces.

2.4.1.1

At N.T.P, one gm-mole of a gas

i.e, N_A molecules occupy $= 22.4\,L = V_g$

But, $= 22400$ cc

Total space taken by molecule $= N_A \cdot \frac{4}{3}\pi r^3$.

$\sim \left(\frac{1}{1000}\right) V_g$.

2.4.2 Potentials.

- $V_{attr} \propto \frac{1}{r^6} \rightarrow$ Long Range (Dominate)
- $V_{rep} \propto \frac{1}{r^{12}} \rightarrow (0<r<1)$ Short Range. (Dom).

2.4.3 Pressure Correction (a)

Reduction in Pr. $\propto d^2$, $d \propto \frac{n}{V}$ ∴ $P_{red} \propto \frac{n^2}{V^2}$ ∴ $P_{id} > P_{real}$

∴ $P_{id} = P + P_r$

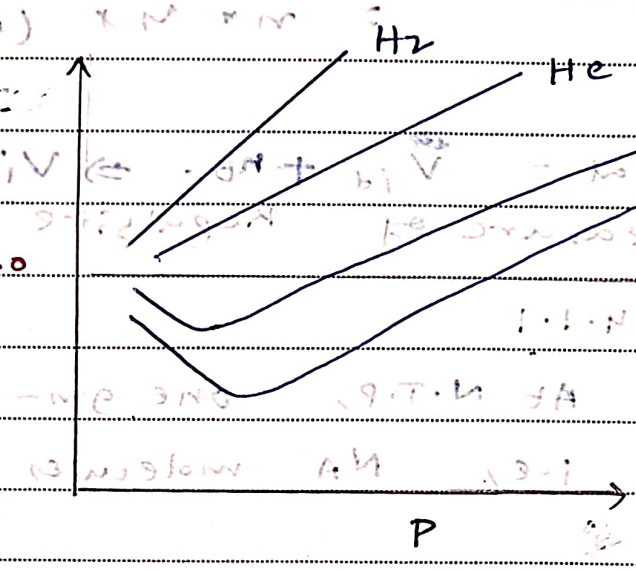
$= P + \frac{an^2}{V^2}$

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$a \rightarrow$ measure of Intermolecular Attraction.

$a \uparrow$ More easily liquifiable

2.5 Qualitative Expl. of Amagat Curve.



2.5.1 $Z = 1$

low P, $(P \rightarrow 0)$ $\bar{v} \rightarrow$ large.

Both V_{attr}, V_{rep} small

$\therefore$ Ideal

2.5.2 $Z > 1$

(H_2)

$a \rightarrow$ small

$\therefore b - \frac{a}{RT} = (+)ve$

$P \uparrow Z \uparrow$

High P, $\rightarrow \bar{v} \downarrow \rightarrow V \downarrow$

$\therefore V_{attr} < V_{rep}$

$\therefore$ Less compressible.

2.5.3 $Z < 1$

a high (CO_2)

$\therefore b - \frac{a}{RT} \rightarrow (-)ve$

$P \uparrow Z \downarrow$

Moderate P, $V_{rep} < V_{attr}$.

$\therefore$ More compressible

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2.6 BOYLE'S TEMP (T_B)

at T_B, $\left[\frac{\partial (PV)}{\partial P}\right]_T = 0$

when $P \to 0$.

It is the temp. at which real gases show ideal behaviour over an appreciable pressure range.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{(for } n=1\text{)}$$

$$\therefore PV = \frac{RTV}{V-b} - \frac{a}{V}$$

$$\therefore \left[\frac{\partial (PV)}{\partial P}\right]_T = \left[\frac{\partial (PV)}{\partial V}\right]_T \left(\frac{\partial V}{\partial P}\right)_T$$

$$= \left[\frac{-RTb}{(V-b)^2} + \frac{a}{V^2}\right] \left(\frac{\partial V}{\partial P}\right)_T \quad \left(\frac{\partial V}{\partial P} \neq 0\right)$$

$$\therefore T_B = \frac{a}{Rb}\left(1 - \frac{b}{V}\right)^2 \simeq \frac{a}{Rb} \quad (P \to 0)$$

2.7 Compressibility Factor (Amagat Curve)

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

$\left(-\frac{ab}{V^2}\right.$ Neglect

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

P.T.O.

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

$$= f(T, P)$$

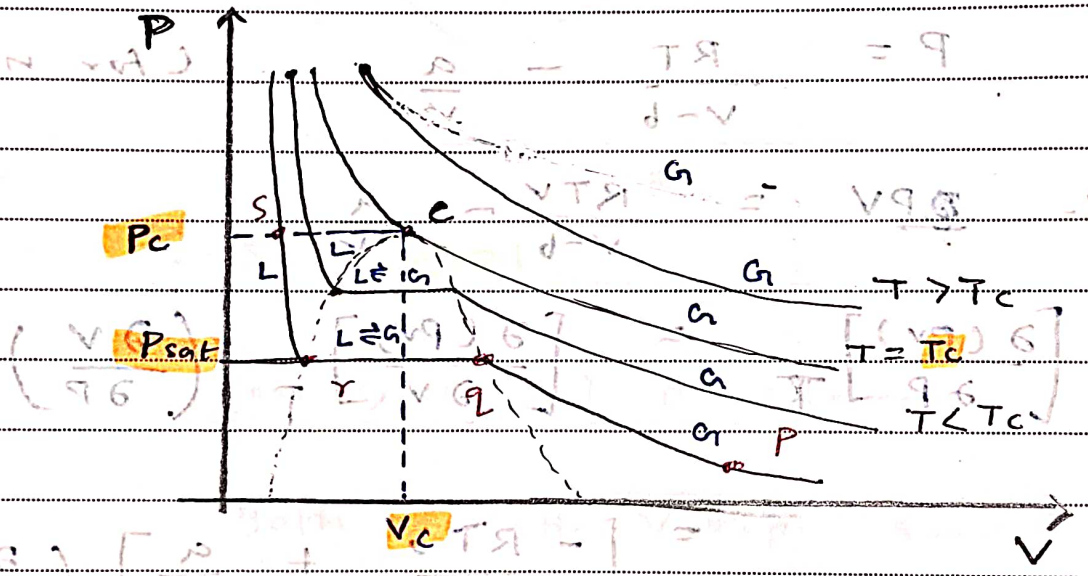
$$y = c_1 T + c_2 \ln(x)$$

At $T = T_B$ $[Z = 1]$

$$\therefore T_B = \frac{a}{Rb} \quad (iv)$$

3. Critical Phenomena:

3.1 Isotherms of Real Gas



P → Behaves like CO_2 at low pressure.

$PV \downarrow$ (Boyle)

(q → r) ≡ P → constant

Although V ↓ (Liquification)

q → CO_2 begins to liquify.

P → Saturation vapour pressure of CO_2

r → All liquid CO_2.

rs → Curve very steep, small V change → large P change.

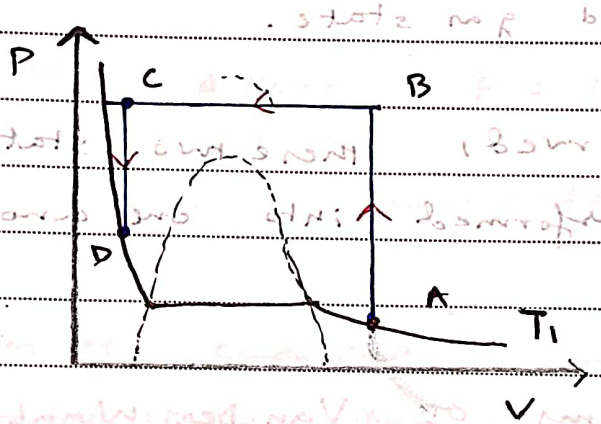
* All conversion DOMS Isothermal.

- saturation pressure ↑, until T_c:
  Temp ↑

- At T_c, plateau shrinks to a point A and this temp → critical temp. (T_c) of CO_2.

- When temp is still increased, isotherm approaches more closely to that of ideal gas, and no liquid is formed.

3.2 Continuity of States



- There is no dividing line b/w the liquid and gaseous states. This fact that it is not always possible, to find a clear line of demarcation to distinguish b/w the two phases, is called Principle of continuity of states.

- We perform the operation, on same isotherm T_1 (A → Gas, D → liquid)

A → B , B → C , C → D :
heat, cool, cool
V = const P = const

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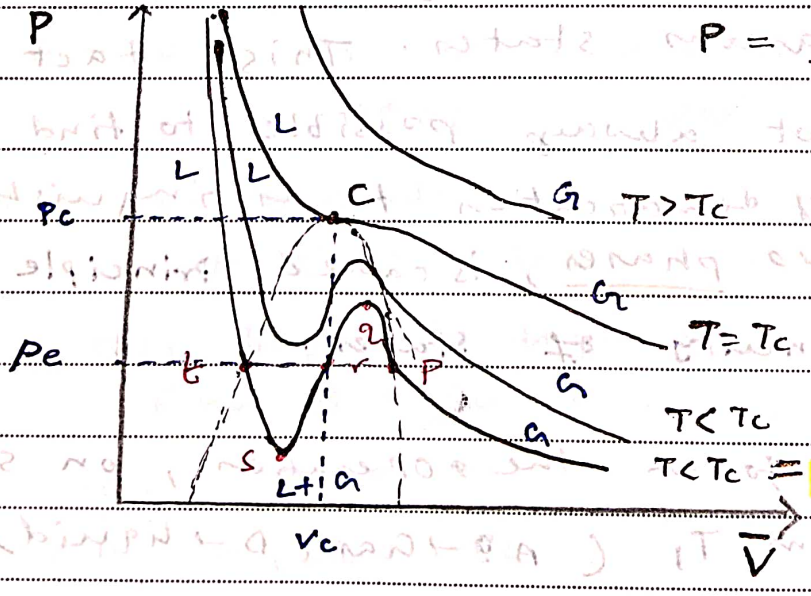
- At no time, in this series of changes did the state point pass thru the 2-phase region condensation in the usual sense did not occur.

∴ D → Highly compressed gas,

But from graph, D should be liquid.
This implies, we can hardly make any difference b/w liq and gas state.

There is observed, these two states of matter can be transformed into one another continuously

3.3 Isotherms of Van Der Waal Eqn



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

Limitations! –

- P q r s t → shows → there are 3 volumes of system ($\bar{V}'$, $\bar{V}''$, $\bar{V}'''$) for a given T and P.
- r q , ↑ shows, ~~more~~ P ↑ , Vol. ↑ (??) unstable → collapse ✗ .

However -

① pq → $P > (P_{vap})_{eq} = P_e$

∴ Points → Supersaturated or supercooled vapour.

② ts → Here $P = (P_e)_{T < T_2}$

So, liquid → Superheated liquid.

The states of supervap & suph. liq. are metastable states, they are unstable, slight disturbance → system revert spontaneously into stable state with the two phases in equilibrium.

3.4 Critical State (C)

3.4.1. Features.

- At C, boundary b/w liq & gas phase disappear
- $\rho_{gas} = \rho_{liq}$.
- P_c, V_c, T_c

3.4.2 Mathematical Deduction:

3.4.2.1

The Van D.W. Eqn can be written in the form.

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

$$\Rightarrow (\bar{V} - \bar{V}')(\bar{V} - \bar{V}'')(\bar{V} - \bar{V}''') = 0 \quad (5)$$

At critical point,

$$\bar{V}' = \bar{V}'' = \bar{V}''' = \bar{V}_c$$

$\therefore$ Eqn.

$$\bar{V}^3 - 3\bar{V}_c\bar{V}^2 + 3\bar{V}_c^2\bar{V} - \bar{V}_c^3 = 0$$

comparing coeff, we can find P_c, V_c, T_c

3.4.2.2.

The point of inflection on the P V/s $\bar{V}$ curve occurs at C.

Thus,

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = 0 \quad \& \quad \left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = 0$$

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

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = \frac{-RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3}$$

& curvature

$$\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = \frac{2RT}{(\bar{V}-b)^3} - \frac{6a}{\bar{V}^4}$$

At critical state,

$$\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3} \quad \& \quad \frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4}$$

&

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}$$

Solving we obtain, Critical constants

$$V_c = 3b \qquad T_c = \frac{8}{27}\frac{a}{Rb} \qquad P_c = \frac{a}{27b^2}$$

($V_c = 3nb$) depends on moles.

3.4.3 Critical coefficient.

$$Z_c = \frac{P_c V_c}{R T_c} = \frac{3}{8} < 1$$

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However for ~~Gas~~ most gases, critical coefficient varies with avg. value = 3.66 ($\neq 8/3$)

We can calculate Van Der Waal constants also,

$$b = \frac{V_c}{3} \qquad a = \frac{27}{64}\frac{R^2 T_c^2}{P_c}$$

$$= 3 P_c \bar{V}_c^2$$

3.5 Law of Corresponding States.

Using the values of a, b we can write, VDW eqn as,

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

$$P = \frac{8 P_c \bar{V}_c T}{3 T_c (\bar{V} - \bar{V}_c/3)} - \frac{27}{64}\frac{R^2 T_c^2}{P_c \bar{V}^2}$$

$$= \frac{3 P_c \bar{V}_c^2}{\bar{V}^2}$$

$$\frac{P}{P_c} = \frac{8 (T/T_c)}{3(\bar{V}/V_c) - 1} - \frac{3}{(\bar{V}/V_c)^2}$$

Defining Reduced variable,

$$\pi = P/P_c \qquad \tau = T/T_c \qquad \phi = V/V_c$$

we can write,

$$\pi = \frac{8\tau}{3\phi - 1} - \frac{3}{\phi^2}$$

4. Kammerlingh - Onnes - Virial Eqⁿ

$$P\bar{V} = RT\left[1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \cdots\right]$$

B, C, D → 2nd, 3rd, 4th ... Virial coefficient.
dependent on T & nature of gas.

Also,

$$P\bar{V} = RT\left[1 + B_1 P + C_1 P^2 + \cdots\right] \quad *$$

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

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

$$(1+\theta)^n = 1 + n\theta + \frac{n(n-1)}{2}\theta^2 + \cdots$$

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

$$\simeq RT\left(1 + \frac{b}{V}\right) - \frac{a}{V}.$$

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

B - 2nd Vir coeff.

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

(Approximation)

The complete curve (accurate) is obtained by Virial form of VDW. eqn.

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2 + \frac{ap^4}{(RT)^4}\left(3b^2 - \frac{2a^2}{(RT)^2}\right)$$

* Limitations of VDW

1) The eqn predict, $V_c = 3b$ but mean value of $V_c = 2b$

2) VDWE suggest, $\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.66$ (not so).

3) $\frac{T_B}{T_c} = \frac{27}{8} = 3.375$, but the value is 2.58.

Explains qualitatively, but it fails to explain.

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KTG

9/4/2023

1.1 Assumptions.

Read from pdf :)

1.2 Idea of Root_Mean- square speed (C_{RMS}).

Let, $\bar{\varepsilon}$ = Average kinetic Energy of gas molecules (N)

where, N_1 molecules have $c_1 \rightarrow \varepsilon_1$

and soon.

$$\bar{\varepsilon} = \frac{N_1\varepsilon_1 + N_2\varepsilon_2 + \dots}{N}$$

$$= \frac{1}{N}\left[\sum_{i=1}^{N} N_i \left(\frac{1}{2} m c_i^2\right)\right]$$

$$= \frac{1}{2} m \left[\frac{\sum N_i c_i^2}{N}\right]$$

$$= \frac{1}{2} m C_{RMS}$$

$$\therefore C_{RMS}\left(= \sqrt{\bar{c}^2}\right) = \sqrt{\frac{N_1 c_1^2 + N_2 c_2^2 + \dots}{N}}$$

$\therefore \bar{\varepsilon}$ & thus C_{RMS} is a measure of temp. (T)

At, $T = 0\,K \rightarrow \bar{\varepsilon} = 0$ $\quad (\bar{\varepsilon} \propto T)$

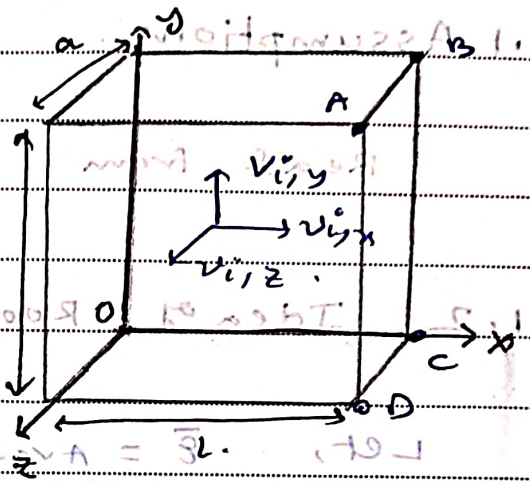
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1.3 Kinetic Equation (P.T.O, move correct)

M-1

Let us take a volume.

$V = abl$.



m = Mass of each molecule.

N = Total no. of Molecules.

c_i = Resultant speed

Let N_i particles (molecules) have speed c_i

where $(c_i)^2 = (v_{i,x})^2 + (v_{i,y})^2 + (v_{i,z})^2$

Now, during collision, (X-direc)

$\Delta P_i = 2m v_{i,x}$

On an avg, $\Delta t = \frac{2l}{v_{i,x}}$.

∴ By N2L, F_{avg} on one face of container, due to i^{th} particle, is (X-direc).

$$F_{avg} = \frac{\Delta P}{\Delta t} = \frac{2m v_{i,x}}{\frac{2l}{v_{i,x}}} = \frac{m v_{i,x}^2}{l}$$

$$\therefore F_{avg} \text{ on } |_{ABCD} = \frac{m}{l} \sum_{i=1}^{N} v_{i}^2{}_x$$

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$$F_{av} = \frac{Nm}{l}\left(\frac{\sum_{i=1}^{N} v_i^2 x}{N}\right)$$

Note, $\frac{\sum x}{N} = \langle x \rangle$ (Avg).

Again, as we have uniform velocity throughout the container.

$$\frac{\sum v_x^2}{N} = \frac{\sum v_y^2}{N} = \frac{\sum v_z^2}{N}.$$

$$\Rightarrow \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle.$$

$$\therefore \frac{\sum (v_i)^2}{N} = \frac{\sum v_{i,x}^2}{N} + \dots$$

$$\Rightarrow \langle c^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$$\Rightarrow \langle v_x^2 \rangle = \dots = \frac{\langle c^2 \rangle}{3} = \frac{c_{RMS}^2}{3}.$$

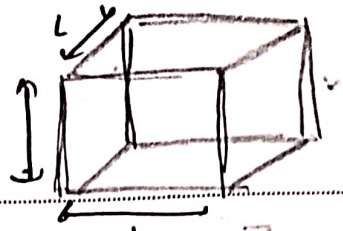
∴ Pressure on $\frac{F}{A}$.

$$\rightarrow \frac{F}{ab} = P = \frac{Nm}{(lab)} \frac{c_{RMS}^2}{3}$$

$$\Rightarrow PV = \frac{1}{3} N m c_{RMS}^2.$$

$$\Rightarrow P = \frac{1}{3} \rho c^2.$$

M-2.



We take a cubical container,

T.S.A. $= 6l^2$

Vol, $V = l^3$

No. of collisions suffered by molecule in unit time b/w the opp. walls $= \frac{v_{i,x}}{l} = \dot{q}$ (x-direc)

$\therefore (F)_i|_x = \frac{dP}{dt} = (\Delta p)\dot{q}$

$= (2mv_{i,x}) \cdot \frac{v_{i,x}}{l} = \frac{2m}{l} v_{i,x}^2$

Total Rate of change of momentum of molecule,

$\therefore (F)_i = \frac{2m}{l} [v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2]$

$= \frac{2m}{l} c_i^2$

$\therefore$ For N_i molecules, $\rightarrow \frac{2m N_i c_i^2}{l}$

Taking all molecules of con.

$\therefore$

$(F)_{container} = \frac{2m}{l} \left[\sum_1^N N_i c_i^2\right]$

$= \frac{2mN}{l} \left[\sum_i^N \frac{N_i c_i^2}{N}\right]$.

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$\therefore$ Pressure, $P = \frac{F}{TSA} = \frac{F}{6L^2}$.

$\therefore P = \frac{2mN}{6L^3} C^2_{RMS}$

$P = \frac{1}{3}\frac{mN}{V} C^2_{RMS}$

$\Rightarrow P = \frac{1}{3}\rho C^2_{RMS}$

1.3.1 Root Mean Square speed :

When $N = N_A$; $R = N_A K_B$

$mN = M_0$ (Molecular wt. of gas)

$RT = VP = \frac{1}{3} M C^2_{RMS}$ $(n = 1)$

$\therefore C_{RMS} = \sqrt{\bar{C}^2} = \sqrt{\frac{3RT}{M_0}} = \sqrt{\frac{3K_BT}{m}}$

1.3.2 KE.

$\bar{\varepsilon} = \frac{1}{2} m \bar{C}^2$ (1 gas)

$\therefore RT = \frac{2}{3} N_A \left(\frac{1}{2} m \bar{C}^2\right) = \frac{2}{3} N_A \bar{\varepsilon}$

$\therefore \bar{\varepsilon} = \frac{3}{2}\left(\frac{R}{N_A}\right) T$ → for 1 molecule.

For N_A molecule, i.e n mole ideal gas

$\bar{\varepsilon} = \frac{3}{2} (nN_A) \frac{R}{N_A} \cdot T$

$\bar{\varepsilon} = \frac{3}{2} nRT$

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1.3.3 Deduction of Gas Laws from Kin Eqn.

We had,

1.3.3.1 $$PV = \frac{2}{3} N_A \bar{E}$$

Now $\bar{E} \propto T$

$\therefore PV \propto T \Rightarrow PV = K'T.$

(moles constant) $P \propto T$

$V \propto T$ Charle's Law

T = constant,

$P \propto \frac{1}{V}$ Boyle's Law.

Now,

1.3.3.2

Let us consider two gases under same P, T, V

Then $PV = \frac{1}{3} m_1 N_1 C_1^2 = \frac{1}{3} m_2 N_2 C_2^2$

Further they will have same $\bar{E}$

$\frac{1}{2} m_1 C_1^2 = m_2 C_2^2.$

dividing $N_1 = N_2$.

It means equal vol. of gases at same T & P contain equal No. of molecules

$\therefore$ Avogadro's Law (Proved)

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1.3.3.3 Graham's Law of Diffusion.

Rate of diffusion of gas is directly proportional to speed (c) of gas.

$r_d \propto c$; $c \propto \sqrt{\frac{RT}{M_0}}$

Thus at given temp.

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

1.4 Heat Capacity

Heat capacity (C) of a substance, is defined as the amount of heat required to raise the temp. of the substance by 1°.

Molar Heat Capacity = Molar Mass × Specific Heat

$C_p = m s_p$

$C_v = m s_v$

$C_p - C_v = R$

$C_p > C_v$, C_p involves mechanical work also.

In general,

$C_p = \frac{3R}{2} + x$

$C_v = \frac{5R}{2} + x$

x = (Rot + Vib) contribution

other term — translational only.

1.4.1 Poisson Ratio,

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5R}{2} + x}{\frac{3R}{2} + x} \qquad 1 + \frac{2}{f}$$

f = Degree of freedom of gas.

$$v_{sound} = \sqrt{\frac{\gamma RT}{M_0}} \Rightarrow \gamma =$$

2. Maxwell Speed Distribution

MSD function is given by

$$F(c) = \frac{1}{n} \frac{dn_c}{dc}$$

n = No. density

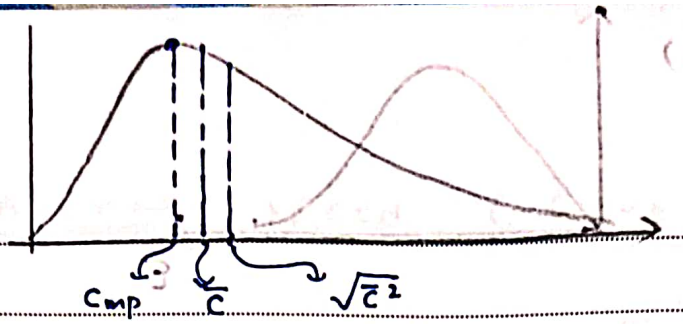
dn_c = No. of molecules within the speed range c to $(c + dc)$

$$F(c) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \cdot e^{-\frac{Mc^2}{2RT}}$$

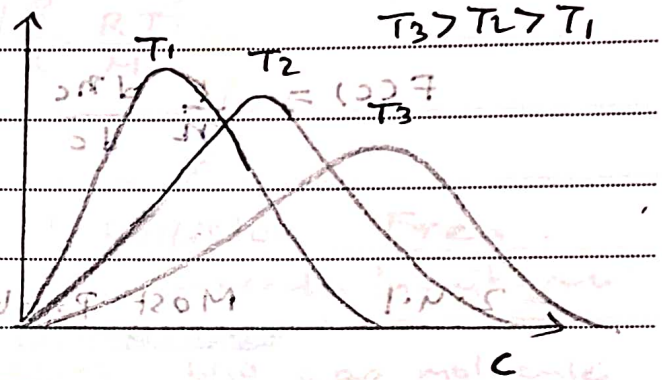
$F(c)$ depends on Molar Mass / Temp.

$$\int_0^\infty F(c) \cdot dc = \text{Total Area under curve} = 1$$

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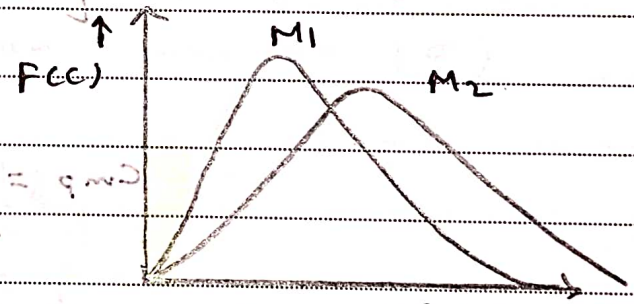
2.1 Effect of Temp.



- $T \uparrow$ curve become more flat
- $T \to \infty$ curve lies on c-axis
- $T \downarrow$, $T \to 0K$, lies on F(c)-axis

↳ Distribution is lost.

2.2 Effect of Mol. Mass (M)



$M_1 > M_2$

Lower Molar Mass
↳ More wider (flat)

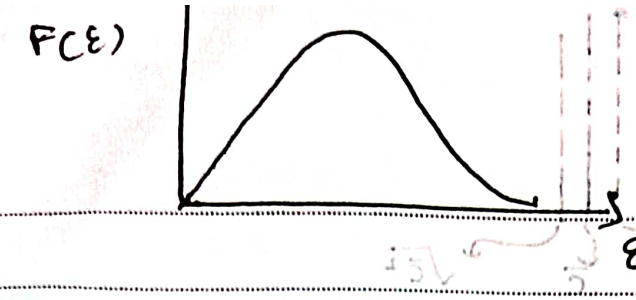
2.3 Kinetic Energy Distribution

We have $\varepsilon = \frac{1}{2} m c^2$. $dc = \frac{d\varepsilon}{mc} = \frac{d\varepsilon}{(2m\varepsilon)^{1/2}}$

we get,

$$F(\varepsilon) = \frac{1}{n}\frac{dn_\varepsilon}{d\varepsilon} = 2\pi \left(\frac{1}{\pi k_B T}\right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/k_B T}$$

↳ independent of nature of gas.



2.4 Derivation of speeds.

We have,

$$F(c) = \frac{1}{n}\frac{dn_c}{dc} = 4\pi \left(\frac{m}{2\pi K_B T}\right)^{3/2} c^2 e^{-\frac{mc^2}{2K_B T}}$$

2.4.1 Most Probable Speed (C_{mp})

At Maxima,

$$\boxed{\frac{d}{dc}\left[F(c)\right]\Big|_{c=c_{mp}} = 0}$$

$$\rightarrow \text{Ac e}^{-\theta}\left[2 - \frac{mc^2}{K_B T}\right] = 0$$

$$c_{mp} = \sqrt{\frac{2K_B T}{m}} = \sqrt{\frac{2RT}{M_0}}$$

2.4.2 Root - Mean Square Speed (C_{RMS})

$$\boxed{C_{RMS} = \sqrt{\frac{\int_0^\infty c^2 dn_c}{\int_0^\infty dn_c}}}$$

$$\Rightarrow \sqrt{\overline{c^2}} = \sqrt{\frac{3K_B T}{m}} = \sqrt{\frac{3RT}{M_0}}$$

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2.4.3 Average speed (C_{Avg} or $\langle C \rangle$)

$$C_{Avg} = \bar{C} = \langle C \rangle = \frac{1}{n} \int_0^\infty c \cdot dn_c$$

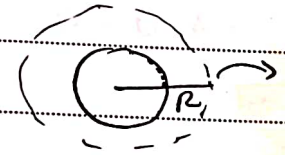
$$\bar{C} = \sqrt{\frac{8}{\pi} \frac{k_B T}{m}} = \sqrt{\frac{8}{\pi} \frac{RT}{M_0}}$$

3. Collision Number & Collision Freq.

C.No. — No. of collision made by gas molecules in unit time

C.f = No. of collision occurring b/w gas molecules in unit time and in unit volume.

(C.f) x Volume = Collision No.



Sphere of influence, $R = \sigma = 2r$.

Dist. of closest approach,

Collision Diameter (σ)

$\bar{C}$ = Average velocity

3.1

- Collision Freq. b/w similar Molecules →

$$Z_{AA} = \frac{1}{\sqrt{2}} \pi n^2 \sigma^2 \bar{C}$$ (per unit vol. per unit time)

3.2 B/w Different molecules.

$$\sigma = \frac{\sigma_A + \sigma_B}{2} \; ; \quad \bar{C} = \sqrt{\bar{C}_A^2 + \bar{C}_B^2}$$

$$= \sqrt{\frac{8 k_B T}{\pi} \left(\frac{1}{m_A} + \frac{1}{m_B} \right)}$$

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Thus $\bar{c}_{AB} = \sqrt{\frac{8 K_B T}{\pi \mu}}$

$\mu = \frac{m_A m_B}{m_A + m_B}$ (Reduced Mass)

Thus $\bar{z}_{A,B} = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8 K_B T}{\pi \mu}} \cdot n_A n_B$

$= \pi \sigma_{AB}^2 \bar{c}_{AB} n_A n_B$

3.3 Mean Free Path (λ):

= Avg. dist. b/w 2 successive collisions of a molecule.

$\lambda = \frac{\bar{c}_1}{\bar{z}_1} = \frac{1}{\sqrt{2}\, n \pi \sigma^2}$

n = No. density $= \frac{N}{V}$

$PV = \left(\frac{N}{N_A}\right) RT$

$\rightarrow n = \frac{P N_A}{RT}$

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

Put this, we can deduce relationship b/w d, P, T

$P \uparrow \lambda \downarrow$, $d \uparrow \lambda \downarrow$, $T \uparrow \lambda \uparrow$ (Physically)

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4. Law of Equipartition of Energy

Total energy of a molecule is equally partitioned among its various degrees of freedom and each degree of freedom (f) contributes $\frac{1}{2} K_B T$ amount of energy

i.e. Total Energy $= \frac{f}{2} K_B T$

$(E_K)_{trans} = \frac{3}{2} K_B T$ ∀ molecules

$= \langle \varepsilon \rangle$

D.O.f — Minimum no. of independent coordinates.

Total D.O.f = $3N - b$ + (Without Vib. D.O.f).

N = Atomicity of molecule

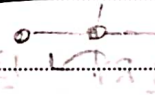
b = No. of constraints.

In our case, we shall take,

Total $f = 3N$

$\therefore (Vib)_f = [3N - (Rot + Trans)]$

Rotational



$\epsilon_{rot} = \frac{1}{2} I \omega_x^2 + \frac{1}{2} I \omega_y^2$ (Linear)



$\epsilon_{rot} = \frac{1}{2} I (\omega_x^2 + \omega_y^2 + \omega_z^2)$ (Non-Linear)

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Vibrational

$$\epsilon_{vib} = \frac{1}{2}\mu(\dot{r})^2 + \frac{1}{2}k(r-r_0)^2$$

Each term contributes $\frac{1}{2}kT$

$\therefore$ Each vib. mode contribut $= 2 \times \frac{1}{2} = k_B T$

Generalising,

$$\bar{U} = N_A \langle \epsilon_t \rangle \quad \& \quad R = N_A k_B$$

$\bar{U}$: Total Avg. Energy per Moles

$\langle \epsilon_t \rangle$: Avg. Energy per molecule

$$\bar{U} = \underbrace{\frac{3}{2}RT}_{\text{Trans}} + \underbrace{\frac{2}{2}RT}_{\text{Rot.}} + \underbrace{(3N-(3+2))RT}_{\text{Vib. (Linear)}}$$

$$\bar{U} = \underbrace{\frac{3}{2}RT}_{\text{Trans}} + \underbrace{\frac{3}{2}RT}_{\text{Rot.}} + \underbrace{(3N-(3+3))RT}_{\text{Vib. (Non-Linear)}}$$

$C_p - C_v = R$, $\quad C_v = \left(\frac{\partial U}{\partial T}\right)_v$, $\quad \gamma = \frac{C_p}{C_v}$

$R = 2$ cal mol^{-1}K^{-1}

Gas	Total D.O.f $= 3N$	Trans D.O.f	Rot. D.O.f	Vib. D.o.f	Total contributions	$\bar{U}$	C_v
Linear CO_2	9	3	2	$9-5=4$	$\frac{3}{2}KT + \frac{2}{2}KT + 4KT$	$\frac{13}{2}RT$	$\frac{13R}{2}$
Bent SO_2	9	3	3	3	$\frac{3}{2}KT + \frac{3}{2}KT + 3KT$	$6RT$	$6R$
Bent (Pyr.) NH_3	12	3	3	6	$\frac{3}{2}KT + \frac{3}{2}KT + 6KT$	$9RT$	$9R$

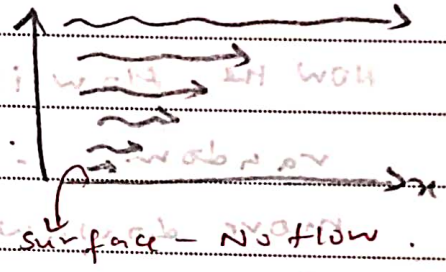
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Note.

Expt.) values matches with theo. values only at high temperatures, as it is a classical theory, not compatible with quantized energy levels.

∴ At High T, quantized Energy levels → continuous ∴ As a result calculated C_p, C_v values matches.

5. Viscosity of Gases.



- Internal friction
- Result of unequal velocity
- Resistance to flow

$$F = -\eta A \frac{dv}{dz}$$

A = Area of contact

$\frac{dv}{dz}$ = velocity gradient.

η = coeff. of viscosity → CGS → 1 Poise = 1 dyne-s/cm².

1N = 10^5 dyne

→ SI → 1 decapoise = 1 Pa-s

5.1 Temp. dependence of viscosity of gases.

For a given particle density n (number density), the following number of particles dN will be found,

$M = m \cdot AN$

$\frac{1}{3} N \cdot AN = R$!!

$$dN = n\,dV = n\,dA\,(\bar{v}\,dt)$$

∴ Particle flux of a directed motion (passing thru an area ⊥r to flow)

$$\dot{n}_A = \frac{dN}{dA \cdot dt} = n \cdot \bar{v}$$

Now the flow is no longer directed (laminar), random ∴ only $\frac{1}{6}^{th}$ of particle will move downwards and diffuse into a gas layer below.



∴ For random motion

$$\dot{n}_A = \frac{1}{6} n \bar{v}$$

$$= \frac{1}{6} n \cdot \sqrt{\frac{8 K_B T}{\pi m}}$$

Putting in eqn.

$$\eta = 2 \dot{n}_A m \lambda$$

Also, $$\lambda = \frac{1}{\sqrt{2}\, n \pi \sigma^2}$$

We obtain

$$\eta = \frac{2}{3} \sqrt{\frac{K_B m T}{\pi^3 \sigma^4}} \rightarrow \eta \propto \sqrt{T}$$

$N_A \cdot m = M$
$R = N_A \cdot K_B$

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Thus temp ↑ viscosity of gas

with Thermal conductivity (K)

$$K = \frac{1}{3} \rho \lambda C_v \bar{v}$$

6. Maxwell Boltzmann Distribution Law

6.1 Barometric Distribution Law

$$P = P_0 e^{-Mgh/RT}$$

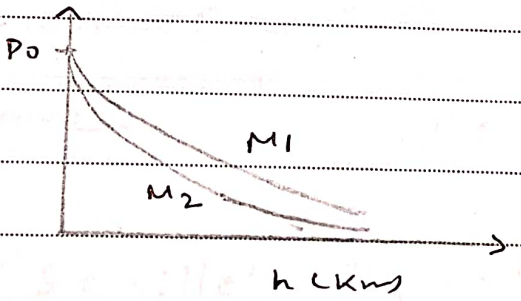
M = Molar mass of air (Avg.)

h = ht. from sea Level

P_0 = 1 atm (at sea level)

Similarly $\therefore n = n_0 e^{-Mgh/RT}$

Number Density



$M_2 > M_1$

6.2 MB Law - Replace $n \to n_0 e^{-Mgh/RT}$

$E = KE + PE$

$$\therefore dn_c = 4\pi n_0 \left(\frac{m}{2\pi K_B T}\right)^{3/2} c^2 e^{-(\frac{1}{2}mc^2 + mgh)/K_B T} \cdot dc$$

$$\therefore dn_c = 4\pi n_0 \left(\frac{m}{2\pi K_B T}\right)^{3/2} c^2 e^{-E/KT} \cdot dc$$

$e^{-E/K_B T}$ → Boltzmann Factor.

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THE LIQUID STATE

15/4/2023

Fluid Flow → Turbulent → $R > 3000$

↓ → Unsteady

Steady / Laminar → $2000 < R < 3000$

$R < 2000$,

Velocity at each & every point remains almost same in both mag. & direction.

* Reynold's Number (R)

$$R = \frac{\rho v d}{\eta}$$

d = diameter of tube.

1. Coeff. of viscosity.

1.1. Newtonian Fluid.

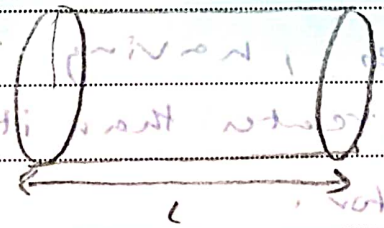
If a fluid flow is such that

(Tangential Force or Viscous Force or Frictional Force) = shearing stress α velocity gradient.

Area

i.e $\frac{f}{A} \alpha -\frac{dv}{dz}$.

1.2. Poiseuille's Equation



- No radial flow
- Newtonian fluid

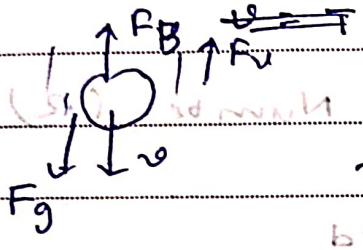
$P_1 > P_2$

$$\frac{dV}{dt} = \frac{\pi (P_1 - P_2) r^4}{8 \eta l}$$

1.3. Stokes' Law

$$F_v = 6\pi\eta r v$$

Only valid for spherical objects of radius 'r'



when $v = v_T$

$$m\ddot{y} = F_g - F_B - F_v = 0$$

1.4. Fluidity

$$\phi = \frac{1}{\eta}$$

Measure of flowing capacity.

- Liquids having heavier & larger molecules flow less easily.
- Impurity ↑, ϕ ↓
- Spherical molecules flow more easily than planar molecules.

1.5. Temperature dependence.

No. of molecules, having a certain energy or greater than it, is given by Boltzmann factor.

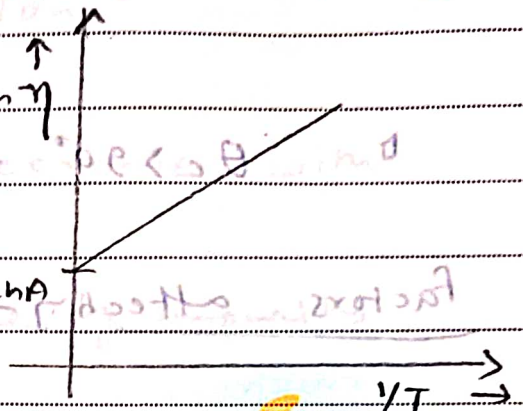
Evis - Viscosity - Activation Energy.

(sufficient energy required to squeeze past intermol. attrn.)

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$\phi \propto e^{-E_{vis}/RT}$

$\Rightarrow \eta \propto e^{E_{vis}/RT}$



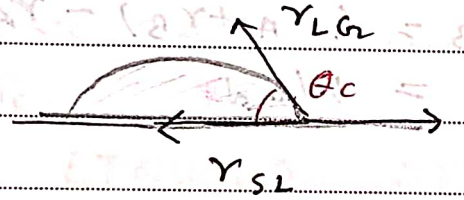
$\Rightarrow \boxed{Ln(\eta) = Ln\,A + \frac{E_{vis}}{RT}}$

A = Prop. Constant.

* Thus Viscosity of liquids decreases with Rise in Temp.

2. Contact Angle & Surface Tension.

2.1 Young's Equation:



Note
If $\theta_c > 150°$
Superhydrophobicity.

γ_{SG} = Solid - vapour interfacial energy.
γ_{SL} = " liquid " "
γ_{LG} = liquid vapour " " (Surface Tension)

Then at the equilbm contact angle θ_c,

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG}\cos\theta_c = 0$$

$$\Rightarrow \boxed{\theta_c = \cos^{-1}\left(\frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}\right)}$$

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II Spreading occurs when $\theta_c < 90°$

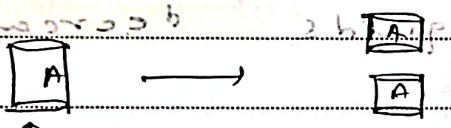
$\cos\theta_c < 0$.

II $\theta_c > 90°$ → No spreading.

Factors affecting — ∘ Nature of solid surface
∘ Nature of liq
∘ Value of Interfacial Tension
∘ Temp of system.

2.2 Forces Work.

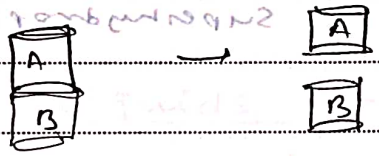
2.2.1 Work of cohesion.



$\Rightarrow W_{AA} = 2(\gamma_A + \gamma_A) - 0$

$W_{AA} = 2\gamma_A = W_c$

2.2.2 Work of Adhesion



$W_{AB} = (\gamma_A + \gamma_B) - \gamma_{AB}$

$= W_{ad}$

2.2.3 Spreading coefficient. Φ

Determines whether liq A will spread over liq B.

$\Phi = W_{ad} - W_c$ ✓ Area.

γ = surface Tension.

$= [(\gamma_A + \gamma_B - \gamma_{AB}) - 2\gamma_A] \times 1$

$\rightarrow \Phi = \gamma_B - \gamma_A - \gamma_{AB}$

$\Phi > 0$ → A spread over B (oil in water)

$\Phi \leq 0$ → No spread, (Hg on Glass).

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2.3 ~~Eötvö~~ ERS Equation

Surface Tension (S) decreases with rise in temp.

- Increases with presence of impurities

Eqn →

$$S = K \frac{(T_c - T - 6)}{(MV)^{2/3}}$$

M = Molar Mass of liquid

MV = Molar Vol. ; V = specific volume of liquid

T_c = critical Temp.

K = Eotvos constant = 2.1×10^{-7} $\frac{J}{(K\text{-}mol^{2/3})}$

Surface Tension = 0 at a temp. below 6 K of T_c.

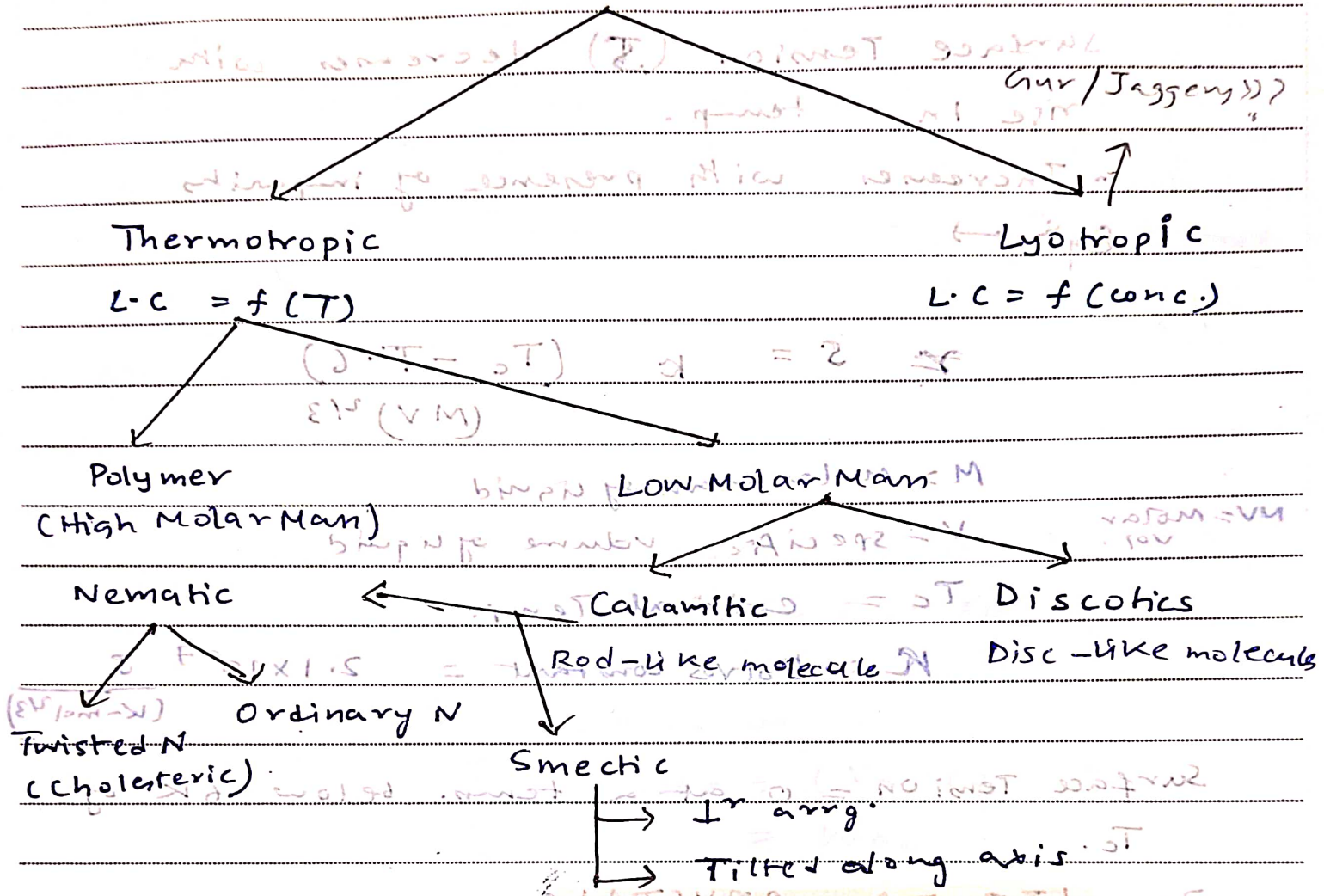
3. LIQUID CRYSTALS.

Crystal → Liquid crystal → Liquid.
(Mesomorphic state)

- properties →
- Exists for small Temp. Range → $\Delta T \simeq 0.5 - 1\,C^\circ$
- Milky, translucent, anisotropic
- occurs because, in some crystal, the ordered arrangement is so great, that thermal agitation ~~cannot~~ is not sufficient to break the lattice.

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3.1 Types :

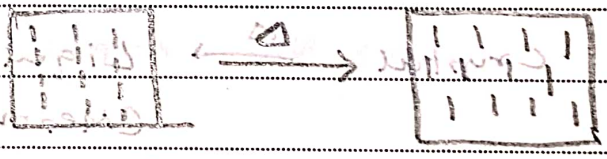


3.1.1 Nematic.

→ Obs by pol. light.

→ Thread-like

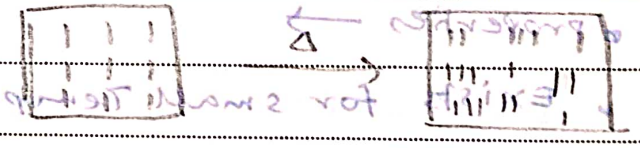
→ Used in LCD



3.1.2 Smectic.

• Like heat, diff planes or sheets slide over one another.

• Obs in pol light & X-Ray.



3.1.3. Cholesteric phase.

• shows colour in polarized light.

4. VAPOUR Phase

Defined as the pr.em. of a liquid in closed container, when

Rate of Evap = Rate of condensation

liq ⇌ gas

4.1 Effect on Temp.

According to clausius a Clayperon Eq^{n}

$\Delta V = V_g - V_l \cong V_g$

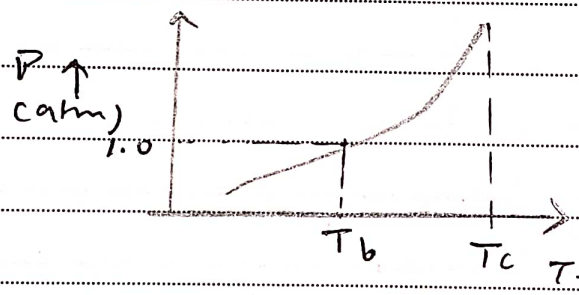
$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} > 0 = \frac{\Delta \bar{H}vap}{T\bar{V}g}$$

$\bar{V}g$ → change in specific volume during the phase transition from liquid to vapour.

$$\frac{dP}{P} = \frac{\Delta \bar{H}vap\, dT}{RT^2}$$

$$\ln P = -\frac{\Delta \bar{H}vap}{RT} + z.$$

T_b = Boiling point, when $P_{vap} = P_{ext}$ (atm)



$\Delta H_{vap} > 0$

For most liquids $\frac{T_b}{T_c} = 0.67 = \frac{2}{3}$

[Temp. in K]

4.2 Relⁿ b/w p (vap. pr) & P (ext. Pressure)

$$V_g dp = V_l dP$$

V_g, V_l - Molar vol.

Assuming ideal gas, [$pV_g = RT$]

$$\frac{dp}{p} = \frac{V_l}{RT} dP$$

$$\rightarrow \ln \frac{p_1}{p_2} = \frac{V_l}{RT}(P_1 - P_2)$$

DOMS