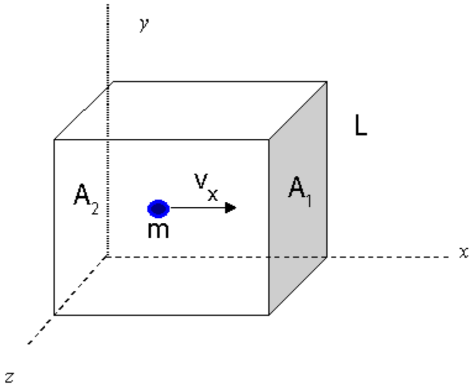
CHB-201: Section (B) – Physical Chemistry-I

(1. Gaseous and Liquid States)

Kinetic theory of gases and ideal gas laws: it is applicable for ideal gas only. Assumptions or postulates of the kinetic molecular theory of gases are given below:

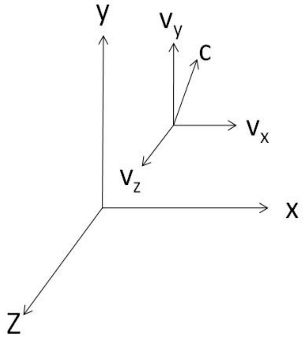
1. Gases consist of large number of minute particles called molecules. The molecules are so small and the actual volume of the molecules is negligible in comparison to the total volume occupied by the gas. They are considered as point masses.
2. Collisions between gas particles are elastic collisions.
3. Gas particles are in constant, rapid, random motion. They therefore possess kinetic energy. The average kinetic energy of the gas particles depends only on the absolute temperature of the system.
4. There are no forces of attraction or repulsion between gas particles.
5. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

Derivation of Kinetic gas equation:



Consider a cubic box of length ***L*** filled with the ***N*** gas molecules with each mass of m. consider one molecule moving with velocity c. velocity c can be resolve along three axes as v_x, v_y, v_z .

Hence, $c^2 = v_x^2 + v_y^2 + v_z^2$



Consider the motion of one molecule moving along the x-axis with velocity v_x Therefore its momentum is mv_x.

The gas molecule collides with the walls. At wall A_1, it collides and the gains momentum mv_x.

Similarly, the molecule collides wall A_2, reversing the momentum i.e., $-mv_x$.

Thus, the change in the momentum is given by

$$\Delta p = mv_x - (-mv_x) = 2mv_x \text{——(1)}$$

Immediately after the collision with wall A_1, the molecule take time L/v_x to collide with wall A_2. Thus, c*hange in momentum per unit time along x axis* = $\Delta p_x/\Delta t$ $= 2mv_x^2/L$ —(2)

The total Change in momentum per unit time along three axes **($\Delta p/\Delta t$)** $= 2mv_x^2/L + 2mv_y^2/L + 2mv_z^2/L$

$= 2m/L\ (v_x^2 + v_y^2 + v_z^2) = 2mc^2/L$

According to Newton's second law of motion the change in momentum per unit time is **Force**.

Force **(F)** $= 2mc^2/L$ —— (3)

The continuous collisions also exert pressure on the wall given by-

Pressure **(p)** ***= Force/Area = F/A*** ***(area of one wall =*** L^2***, there are six walls so total area of walls is 6*** L^2 ***)***

Pressure (p) $= \dfrac{\{2mc^2/L\}}{6L^2} = \dfrac{mc^2}{3L^3} = \dfrac{mc^2}{3V}$ (volume of cube (V) $= L^3$) —(4)

We know that the gas is made of N number of molecules and move in all possible directions.

Thus, the total pressure (***P***) exerted by the collision of N number of gas molecules is given by-

$$P = \frac{mNc^2}{3V} \quad \text{or} \quad PV = \frac{mNc^2}{3} \quad \text{------- (5)}$$

Equation (5) known as ***kinetic gas equation***

Derivation of gas laws from kinetic gas equation

Boyle's law: from kinetic gas equation, $PV = \dfrac{mNc^2}{3}$

or, $PV = \frac{2}{3}N\dfrac{mc^2}{2} = \frac{2}{3}N.(K.E.)$ *where* $\dfrac{mc^2}{2}$ is kinetic energy (K.E.)

at constant temperature K.E. is constant and N is also constant

Hence, ***PV = constant*** (at constant temperature)

This is Boyle's law

Charle's law: $PV = \frac{mNc^2}{3} = \frac{2}{3}\frac{N}{P}\frac{mc^2}{2}$

or, $V = \frac{2}{3}\frac{N}{P}\frac{mc^2}{2} = \frac{2}{3}\frac{N}{P}K.E.$

at constant pressure, $\frac{2}{3}\frac{N}{P}$ is constant

V = constant x K.E.

K.E. is depend on temperature,

so, ***V α T*** *(at constant pressure)* [This is Charle's law]

Avogadro's law: For any two gases, the kinetic gas equation may be written as

$P_1V_1 = \frac{2}{3}N_1\frac{m_1c_1^2}{2}$ **and** $P_2V_2 = \frac{2}{3}N_2\frac{m_2c_2^2}{2}$

when P and V of two gases are same i.e. $P_1=P_2$ *and* $V_1 = V_2$

Then, $P_1V_1 = P_2V_2$

or, $N_1\frac{m_1c_1^2}{2} = N_2\frac{m_2c_2^2}{2}$ -----------------*(1)*

at constant temperature the mean molecular kinetic energy of both gases are same

$$\frac{m_1c_1^2}{2} = \frac{m_2c_2^2}{2}$$

Hence, from equation (1) $\boldsymbol{N_1 = N_2}$ (at constant T, P, V)

This is Avogadro'law.

Types of molecular velocities: Three types of molecular velocities are reckoned in the study of gases.

1. **The most probable velocity (c_p):** c_p is defined as the velocity possessed by maximum number of molecules at given temperature.

   $c_p = \sqrt{\frac{2RT}{M}}$ (R is gas constant, T is absolute temperature and M is molar mass of gas)
2. **Average Velocity (<c>):** The average velocity is the sum of the velocities of all of the molecules divided by the number of particles at a given temperature.

   $$< c >= \sqrt{\frac{8RT}{\pi M}}$$
3. **Root mean square Velocity ($<c^2>^{1/2}$):** The **Root mean square** velocity is square root of the average velocity-squared.

   $< c^2 >^{1/2} = \sqrt{\frac{3RT}{M}}$

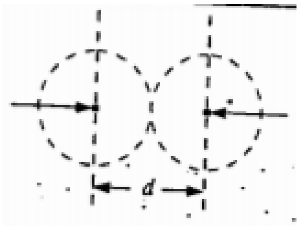
The increasing order of velocity: c_p < (<c>) < ($<c^2>^{1/2}$)

Question: Show that the velocity 'c' in kinetic gas equation is root mean square velocity.

Collision Parameters

Collision Diameter: The distance between the centers of two molecules at the time of their closest approach is known as collision diameter. It is denoted by 'd'.

The volume $\frac{4}{3}\pi d^3$ is known as effective volume of the molecule.



Collision Cross-section :- When two molecule collide, the effective area of target is πd^2. The quantity πd^2 is called the Collision Cross-Section (σ) of the molecule.

$$\boxed{\sigma = \pi d^2}$$

Collision Number :- Collision number is defined as the "number of collisions" per unit time by a single molecule. It is indicated by the symbols of Z_1.

$$\boxed{Z_1 = \sqrt{2}\,\pi d^2 \langle c \rangle \rho}$$

where d is collision diameter, $\langle c \rangle$ is average velocity $\langle c \rangle = \sqrt{\frac{8RT}{\pi M}}$,

and ρ is the number density. $\left\{ \rho = \frac{N}{V} \right.$ ie number of molecules per unit volume (V) of gas. $\left. \right\}$

Collision frequency :- Collision frequency is the number of molecular collisions occuring per unit time per unit volume of the gas.

Each collision involves two molecules, so the number of collisions of like molecules occuring per unit time per unit volume of gas is given by

$$Z_{11} = \frac{1}{2} \times \text{collision number} \times \text{number density}$$

$$= \frac{1}{2} \times \sqrt{2}\,\pi d^2 \langle c \rangle \rho \times \rho$$

$$\boxed{Z_{11} = \frac{1}{\sqrt{2}}\,\pi d^2 \langle c \rangle \rho^2} \quad \text{—①}$$

Z_{11} is the collision frequency of like molecules.

If collision occuring between type 1 and type 2 molecules i.e. molecules are different Then collision frequency

$$\boxed{Z_{12} = \frac{1}{\sqrt{2}}\,\pi d_{av}^2 \langle c \rangle \rho_1 \rho_2} \quad \text{—②}$$

$d_{av} = \frac{d_1 + d_2}{2}$

ρ_1, ρ_2 are number density of type 1 and type 2 molecules, respectively

for an ideal gas $PV = nRT = n N_A k_B T$ (n = number of moles, N_A = Avogadro number)

or $PV = N k_B T$ $\{N$ = Total number of molecules of gas $= n N_A\}$

or $\frac{N}{V} = \frac{P}{k_B T}$

or $\rho = \frac{P}{k_B T}$

Put the value of ρ in equation 1.

$$\boxed{Z_{11} = \frac{1}{\sqrt{2}}\,\pi d^2 \langle c \rangle \left(\frac{P}{k_B T}\right)^2}$$

Mean Free Path (λ):- It is defined as the mean distance travelled by a gas molecule between two successive collisions. It is denoted by λ.

$$\lambda = \frac{\text{average velocity}}{\text{Collision number}} = \frac{\langle c \rangle}{Z_1} = \frac{\langle c \rangle}{\sqrt{2}\,\pi d^2 \langle c \rangle \rho}$$

$$\text{or} \quad \lambda = \frac{1}{\sqrt{2}\,\pi d^2 \rho} \qquad \left\{ \because \rho = \frac{P}{k_B T} \right.$$

$$\therefore \boxed{\lambda = \frac{k_B T}{\sqrt{2}\,\pi d^2 P}}$$

For ideal gas $PV = N k_B T$

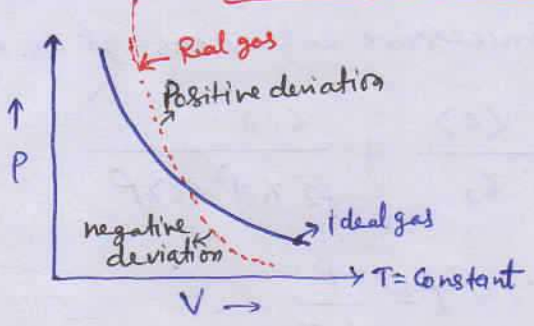
$$\text{or} \quad \frac{T}{P} = \frac{N k_B}{V}$$

$$\frac{T}{P} = \text{Constant} \quad \left\{ \begin{array}{l} \text{if volume is Constant} \\ \text{then } N, k_B, V \text{ are constant} \end{array} \right.$$

* ie in a sample of Constant volume, the pressure (P) is proportional to Temperature (T), so $\frac{T}{P}$ remains Constant when the Temperature (T) is increased. Therefore the mean free path (λ) is independent of the Temperature (T) at fixed volume.

* if Temperature (T) is constant then $\lambda \propto \frac{1}{P}$
ie, with increasing pressure λ decreases.

Real gas (Non-ideal gas)



if $V_{Real} > V_{ideal}$ Then Positive deviation

$V_{Real} < V_{ideal}$ Then negative deviation

for ideal gas $PV = RT$ — ① At all condition of T & P

for Real gas $PV = ZRT$ — ② Z is known as compressibility factor

$$Z = \frac{PV}{RT}$$

* For ideal gas $Z = 1$ ie, $PV = RT$

* For Real gas $PV \neq RT$ ie $Z \neq 1$

$Z \neq 1$

Case 1: if $Z > 1$
- * Positive deviation
- * $V_{Real} > V_{ideal}$
- * Repulsive force dominating

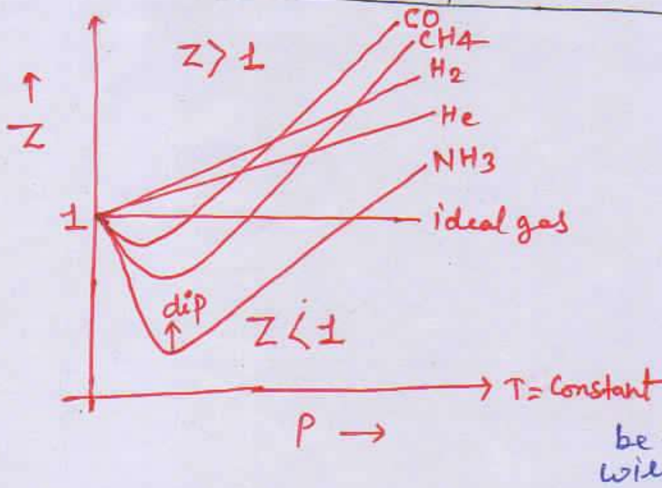
exa: H_2, He

* only H_2 and He shows +ve deviation due to its small mass and small volumes.

Case 2: $Z < 1$
- * Negative deviation
- * $V_{Real} < V_{ideal}$
- * Attractive force dominating

exa: CO, CH_4, NH_3

Variation of Z with Pressure :-



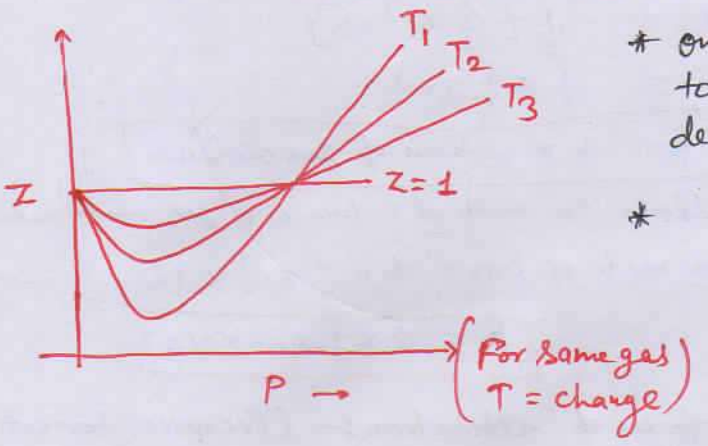
* only H_2 and He shows positive deviation at all pressure and their graph is straight line.

* Remaining all gases shows negative as well as positive deviation and their graph is of curvature nature.

* At low pressure gases shows negative deviation and at high pressure shows +ve deviation.

* Higher is the dip of the curve more will be the deviation from ideal behavior and more will be the attractive force between gas molecules.

Variation of Z with Temperature :-



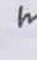
* on increasing the temperature gases approaches to ideal behaviour ie dip of the curve decreases.

* $T_1 < T_2 < T_3$

Reason of deviation from ideal behaviour

There are Two reason:

① ideal gas molecules are point masses but Real gas molecules are rigid spherical particle which have significant volume.

ideal gas	Real gas
	
Point mass	Rigid spherical particle.

② There is no force of attraction between ideal gas molecules but Real gas molecules have significant force of attraction between them.

Vander Waals Equation of state

In 1873, Vander Waals proposed equation of state for a real gas. The two correction term introduced by Vander Waals are describe below.

① Correction due to volume of gas molecules :- Under condition of high pressure, the volume occupied by the gas molecules will no longer be negligible in comparison with the total volume of gas. So actual volume of gas is the volume available for free movement

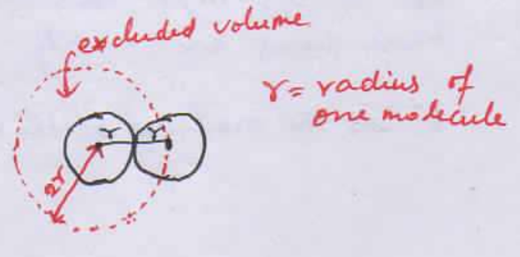
$V_{actual} = V -$ Volume occupied by gas molecules

$\boxed{V_{actual} = V - b}$ (b is known as excluded volume or co-volume; b is the volume occupied by 1 mole of gas)

For n mole of gas

$\boxed{V_{actual} = V - nb}$

Excluded Volume (b) :- Excluded volume is the volume between the molecules of the gas which cannot be available for other molecules for free movement.



Volume of one gas molecule $= \frac{4}{3}\pi r^3$

Excluded volume by Two molecules = $\frac{4}{3}\pi(2r)^3 = \frac{4}{3}\pi r^3 \times 8$

Excluded Volume by one molecule = $\frac{1}{2}\left[\frac{4}{3}\pi r^3 \times 8\right]$

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

$\boxed{\text{Excluded volume by one molecule} = 4 \times \text{volume of gas molecule}}$

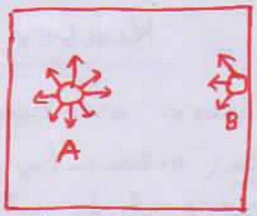
Thus, excluded volume is four times the actual volume of gas molecule.

Excluded volume occubied by one mole of gas = $4 \times \frac{4}{3}\pi r^3 \times N_A$

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

② Correction due to intermolecular forces of attraction:– (Pressure Correction)–

Pressure is due to collision of molecules with the walls of container. At high pressure the force of attraction between molecules are not negligible.



Let us consider two molecules, one is midst of container (A) and another one is near to the wall of container (B). The resultant attractive force on 'A' molecule due to other neighbouring molecules is zero. However, the molecule (B) near to wall of container experiences attractive force from the neighbouring molecules. Hence, it will strike the wall with a lower velocity and exert lower pressure than if there was no force of attraction. So it is necessary to add pressure correction factor 'p' to the pressure of gas 'P'. Therefore the correct pressure is $P+p$.

Calculation of 'p':– The pressure correction factor 'p' depend on the number of molecules collide with the wall and force of attraction exerted on molecule. Both depend on density of gas (ρ).

$$p \propto \rho^2 \Rightarrow p \propto \frac{1}{V^2} \Rightarrow \boxed{p = \frac{a}{V^2}} \text{ (for 1 mole of gas)}$$

$$\boxed{p = \frac{an^2}{V^2}} \text{ (for n mole of gas)}$$

'a' is a constant which depend on nature of gas.

Hence Vander Waals equation

$$\boxed{\left(P + \frac{a}{V^2}\right)(V-b) = RT} \text{ For one mole of gas.}$$

$$\boxed{\left(P + \frac{an^2}{V^2}\right)(V-nb) = nRT} \text{ For n mole of gas.}$$

Physical significance of 'a' and 'b':–

'a' is measure of attractive forces between the molecules. If the value of 'a' is high then more attractive forces works between them. It means these gases are easily liquefied.

'b' is the measure of the volume excluded by one mole of gas.

Discussion of the Vander waals equation:-

① when the Pressure is low:- At low pressure b is negligible ie $b \simeq 0$
So $V - b = V$

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

$$\text{or } \frac{PV}{RT} = 1 - \frac{a}{VRT} \quad \text{Or } Z = 1 - \frac{a}{VRT} \text{ — ①} \left\{ \because Z = \frac{PV}{RT} \right.$$

It means $Z < 1$ (-ve deviation), molecular attraction dominate
when $T \to \infty$ then $\frac{1}{T} \to 0$

From equation ① $Z = 1$ ie $PV = RT$

ie, at low pressure and high temperature real gases approaches to ideal gas behaviour.

② when the pressure is high:- At high pressure $\frac{a}{V^2}$ is small hence the pressure correction term can be ignore ie, $\left(P + \frac{a}{V^2}\right) \simeq P$

from the vander waals equation $P(V-b) = RT \Rightarrow PV - Pb = RT$

or $PV = RT + Pb$ or $\frac{PV}{RT} = 1 + \frac{Pb}{RT}$ or $Z = 1 + \frac{Pb}{RT}$ ie $Z > 1$

It means at high pressure gases shows +ve deviation and molecular size dominate.

③ Exceptional behaviour of Hydrogen and Helium:- Due to very small mass of H_2 and He, the attractive force between their molecules are very small ie 'a' is very small $a \simeq 0$ $P + \frac{a}{V^2} \simeq P$

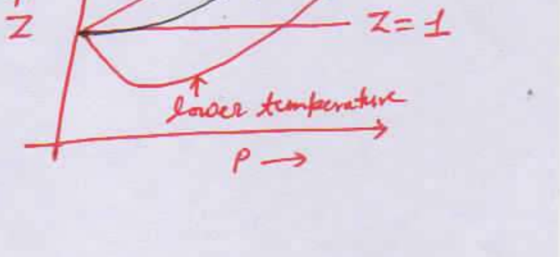
$P(V-b) = RT$ or $PV = RT + Pb$ or $Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$ ie $Z > 1$

It is the reason why H_2 and He shows +ve deviation.

Boyle Temperature (T_B).

Boyle's temperature or Boyle point is the temperature at which a real gas starts behaving like an ideal gas over a particular range of pressure.

It is given by expression $\boxed{T_B = \frac{a}{bR}}$



Determination of Critical Constant by vander waals gas Equation:-

For one mole of a gas, the van der waals equation

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT \qquad \{ V_m \text{ is the molar volume of gas}$$

$$\Rightarrow (PV_m^2+a)(V_m-b)=RTV_m^2$$

$$\Rightarrow PV_m^3+aV_m-PbV_m^2-ab=RTV_m^2$$

$$\Rightarrow PV_m^3-(bP+RT)V_m^2+aV_m-ab=0$$

$$\Rightarrow V_m^3-\left(b+\frac{RT}{P}\right)V_m^2+\frac{a}{P}V_m-\frac{ab}{P}=0 \quad \text{——①}$$

At critical point $P=P_c$ and $T=T_c$

$$V_m^3-\left(b+\frac{RT_c}{P_c}\right)V_m^3+\frac{a}{P_c}V_m-\frac{ab}{P_c}=0 \quad \text{——②}$$

At critical point all three roots are equal ie $V_m=V_c$

or $V_m-V_c=0$

or $(V_m-V_c)^3=0$

$$V_m^3-3V_cV_m^2+3V_c^2V_m-V_c^3=0 \quad \text{——③}$$

Comparing equation ② & ③.

$$b+\frac{RT_c}{P_c}=3V_c \quad \text{——④} \qquad \frac{a}{P_c}=3V_c^2 \quad \text{——⑤} \qquad \frac{ab}{P_c}=V_c^3 \quad \text{——⑥}$$

From equation ⑤ devide by ⑥ $\quad \frac{1}{b}=\frac{3}{V_c} \Rightarrow \boxed{V_c=3b}$

Putting the value of V_c in equation ⑤.

$$\frac{a}{P_c}=3\times(3b)^2 \Rightarrow \boxed{P_c=\frac{a}{27b^2}}$$

Putting the value of P_c and V_c in equation ④

$$b+\frac{RT_c}{a}\times 27b^2=3\times 3b \Rightarrow \boxed{T_c=\frac{8a}{27Rb}}$$

Thus, knowing the critical constants of a gas, it is possible to calculate the van der waals constants and vice versa.

Question:- Calculate Compressibility factor (z) under critical condition.

$$Z=\frac{PV}{RT}=$$

Under critical condition $Z=\frac{P_cV_c}{RT_c}=\frac{1}{R}\times\frac{a}{27b^2}\times 3b\times\frac{27Rb}{8a}=\frac{3}{8}=0.375$

Law of Corresponding states or Reduced equation of states:-

Let $\frac{P}{P_c} = P_r$, $\frac{V}{V_c} = V_r$ and $\frac{T}{T_c} = T_r$ where P_r, V_r and T_r Called the reduced pressure, the reduced volume and the reduced temperature, respectively.

substituting in Vanderwaals equation for one mole of a gas

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

$$\left(P_r P_c + \frac{a}{V_r^2 V_c^2}\right)(V_r V_c - b) = R T_r T_c \quad ①$$

Put $V_c = 3b$, $T_c = \frac{8a}{27Rb}$ and $P_c = \frac{a}{27b^2}$ in equation ①

$$\left(P_r . \frac{a}{27b^2} + \frac{a}{V_r^2 9b^2}\right)(V_r 3b - b) = R T_r \frac{8a}{27Rb}$$

$$\Rightarrow \frac{a}{27b^2}\left(P_r + \frac{3}{V_r^2}\right) b\,(3V_r - 1) = T_r \frac{8a}{27b}$$

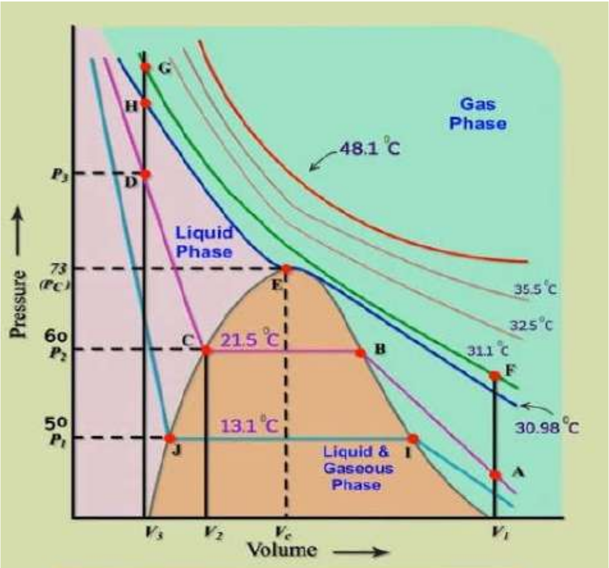
$$\Rightarrow \boxed{\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r}$$

This equation known as Reduced equation of state.

This equation involves neither R not van der Waals Constant a, b. Hence it is general equation applicable to all gases independent of its nature.

If Two or more substances have the same reduced temperature and the same reduced Pressure, they would have the same reduced volume. This statement is known as the principal of corresponding states.

Liquefaction of gases (Critical Phenomenon)



Isotherms of Carbon Dioxide at Various Temperatures

Thomas Andrews in his experiment plotted the graph between the Pressure and Volume at a given constant temperature (P-V isotherm). On studying the isotherm of Carbon dioxide he found that on increasing the pressure gas shows the tendency of liquefaction. On increasing pressure, along the curve AB, Carbon dioxide exist as gas; along BC, it exists partly as gas and partly as liquid; while along CD, it exists entirely as liquid.

On increasing temperature he found that tendency of gas for liquefaction decreases. On continuously increasing the temperature a point (E) come where gas and liquid cannot be distinguished. This point is known as Critical Point and P,V,T corresponding to this point are known as critical pressure (Pc), critical volume (Vc) and critical temperature (Tc). At critical point density of gas becomes equal to density of liquid i.e. their property becomes same. Above critical point gas cannot be liquefied.

Before critical point, **slope of curve** $\frac{dP}{dV} < 0$

At critical point, **slope of curve** $\frac{dP}{dV} = 0$

Critical Temperature (Tc): It is the maximum temperature above which gas cannot be liquefied but below this gas can be liquefied.

Critical Pressure (Pc): It is the minimum pressure required to liquefied the gas

Critical Volume (Vc): Volume occupied by one mole of gas at critical pressure (Pc) and critical temperature (Tc) is known as critical volume (Vc).

Question: For a gas, Pc = 1.5 atm, Tc= 320 K, predict in which of the following conditions liquefaction will take place.

(a) P = 2 atm, T = 300K (b) P =1 atm, T = 330K (c) P = 2 atm, T = 360K (d) P =1.5 atm, T = 310K

Answer: Only at condition of (a) and (d) gas can be liquefied.

Determination of *Tc, Pc* and *Vc*

Determination of *Tc* and *Pc*: This method is based on the principal that at the Tc, the surface of separation between the liquid and vapour disappears i.e. liquid and vapour cannot be distinguished.

The liquid is taken in vessel V enclosed in glass jacket J (see Fig.), the temperature of liquid is maintain by the thermostat. The vessel V is also attach with manometer M for pressure determination. For Tc measurements, the temperature of liquid is raised gradually until the surface of separation between the liquid and vapour disappears. This temperature is noted (say T_1). The liquid is then cooled gradually until cloudiness due to the condensation of vapour appears again. This temperature is also noted (say T_2). The mean of the two temperatures gives *Tc*. i.e. **$Tc = (T_1 + T_2)/2$**

The mean of the pressures corresponding to the two temperatures (at T_1 *and* T_2) gives the value of *Pc*.

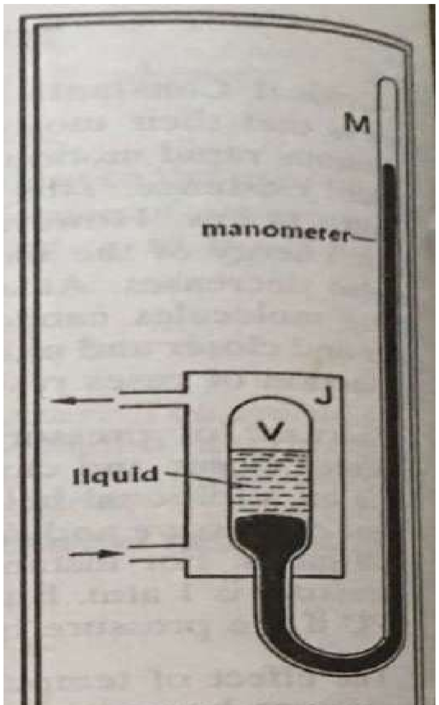
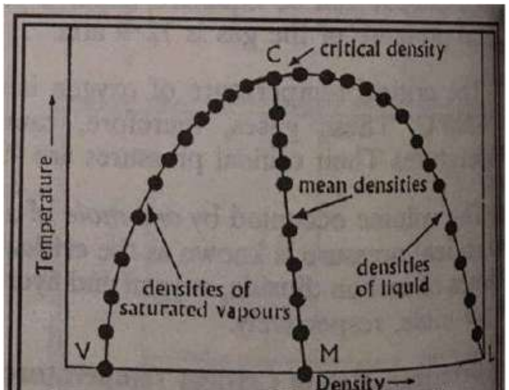


Fig. 8. Determination of critical temperature and critical pressure.

Determination of critical Volume: Critical volume (*Vc*) is measured by density measurements. In this, the densities of liquid and its saturated vapour are plotted with temperature. The densities of saturated vapour increases with increasing temperature (curve VC) but densities of liquid decreases with increasing temperature (curve LC). The point C where the two curves meet gives the critical density. This point is not sharp. The mean densities are then plotted against temperature. A straight line MC is obtained. The point C where this line cuts the curve VCL gives the critical density. The critical volume is then obtained by dividing the molar mass by critical density.

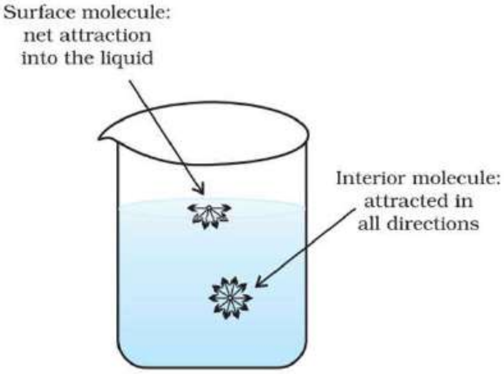
Vc **= Molar mass/critical density**



Determination of the critical volume.

The Liquid State

A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (see Fig.), due to the molecules below it. Since there are no molecules above it.



Forces acting on a molecule on liquid surface and on a molecule inside the liquid

Thus, liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy.

Surface Tension: The force that tends to contract the surface of a liquid known as surface tension. Surface tension, represented by the symbol $\boldsymbol{\gamma}$, is measured in force per unit length. Its SI unit is newton per meter but the cgs unit of dyne per centimeter is also used. The surface tension of water is 72.8 dyne/cm at 20^{o}C.

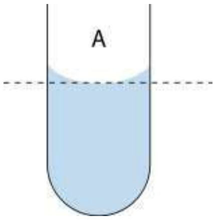
Surface tension is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the cohesive forces of the surface layer.

Capillary Action

Cohesion: The attraction between the like molecules in liquid is known as cohesion.

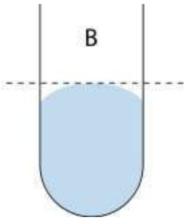
Adhesion: The attraction between the liquid and walls of the capillary is known as adhesion.

Case A: if, adhesion > cohesion



The liquid is said to wet the wall. This is happen in case of water and many other liquids. The meniscus is concave.

Case B: if, adhesion < cohesion



The liquid does not wet the wall. This is happening in case of mercury. The meniscus is convex.

Surface active agents (Surfactants): The substance which lowers the surface tension of the liquid is known as surface active agents. Exa: Soaps, detergents, shampoo etc.

Effect of Temperature on Surface Tension: From the Eotvos equation: $\gamma(M/\rho)^{2/3} = k(T_c - T)$

Where M is molar mass, ρ is density, Tc is critical temperature and k is constant. From the equation, it is clear that surface tension decreases with increase in temperature. This decreasing phenomenon occurs due to lowering of intermolecular force of attraction or cohesive force between liquid molecules as temperature increases.
When **$T = T_c$, $\gamma = 0$, i.e. at critical temperature surface tension of liquid is zero.**

Interfacial Tension: If two immiscible liquids are present one above the other in a vessel. Then, the force acting per unit length along the interface is called interfacial tension.

Surface tension of a liquid is the force acting along the surface of separation between the liquid and its vapour. However, interfacial tension is the force acting along the surface of separation of two immiscible liquids contact to each other.

Methods of Surface Tension Measurements: The following methods are used for surface tension measurements.

1. Capillary rise method
2. Stallagmometer method – drop weight method
3. Torsion method by Tensiometer

1. Capillary rise method: suppose a liquid of density ρ, rises in a capillary of radius r through a height h.

The total force (F) due to surface tension raising the liquid upward = γ x inside circumference of capillary = $2\pi r\gamma$ ------(1)

Downward gravity force = $mg = V\rho g = \pi r^2 h\rho g$ ---(2) (Volume $V = \pi r^2 h$)

At equilibrium: $2\pi r\gamma = \pi r^2 h\rho g$

$\boldsymbol{\gamma = rh\rho g/2}$ ------(3)

This equation is valid when contact angle $\theta = 0$,

if the contact angle is not zero then upward force will be $2\pi r\gamma\cos\theta$. In this case the surface tension would be

$\boldsymbol{\gamma = rh\rho g\cos\theta/2}$ --------(4)

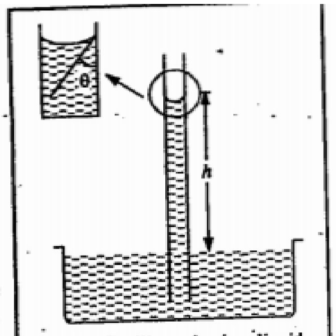


Fig. 7. Capillary rise in a liquid.

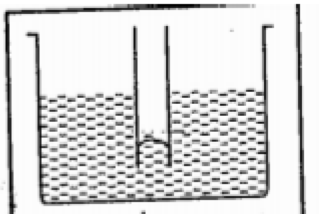


Fig. 8. Capillary depression in mercury

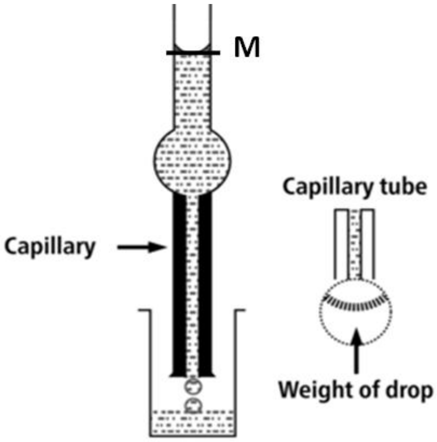
If capillary is dipped in mercury, mercury does not rise in it. The meniscus is lowered by the height –h. this is because of the contact angle θ between glass and mercury is 180°. so, cos180° = -1, hence according to equation (4) h would be negative.

Question: If water at 25°C rises through 6.36 cm in a capillary of radius 0.2 mm. What will be the surface tension at that temperature? (Density of water = 0.997×10^3 kgm^{-3})

Answer: $\gamma = rh\rho g/2 = (.02\ cm \times 6.36\ cm \times 0.997\ gcm^{-3} \times 981\ cms^{-2})/2 = 62.20$ dyne/cm

2. Stallagmometer method – drop weight method: The stalagmometric method is one of the most common methods used for the surface tension determination. In this method the surface tension of unknown liquid is compared to a reference liquid of known surface tension (typically water). Liquid is filled up to the mark M and the number of falling drops counted of both liquids.

The drop falls when its weight w just exceeds the force of surface tension. At equilibrium



$w = mg = 2\pi r\gamma$ (m is the mass of one drop, r is the radius of drop at the end of capillary tube)

For drop of two liquids (one is water and other is unkown)

$w_1 = m_1g = 2\pi r\gamma_1$ (for first liquid i.e. water)

$w_1 = m_2g = 2\pi r\gamma_2$ (for second unknown liquid)

Hence $\frac{w1}{w2} = \frac{\gamma 1}{\gamma 2}$

Let n_1 and n_2 be the numbers of drops formed from the same volume V of the two liquids. Then,

Mass m_1 of a single drop of liquid 1 = $\frac{V\rho 1}{n1}$

Mass m_2 of a single drop of liquid 2 = $\frac{V\rho 2}{n2}$, ρ_1 and ρ_2 is density of liquids

Then $w_1 = V\rho_1 g/\ n_1$

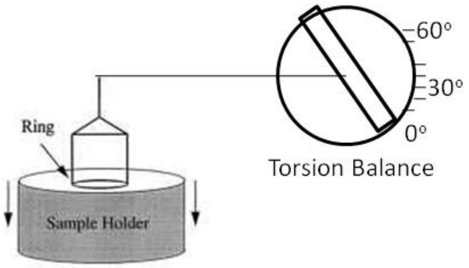
Then $w_2 = V\rho_2 g/\ n_2$

$$\frac{w1}{w2} = \frac{\gamma 1}{\gamma 2} = \frac{V\rho 1gn2}{V\rho 2gn1}$$

$$\frac{\gamma 1}{\gamma 2} = \frac{\rho 1n2}{\rho 2n1}$$

Determined the relative density of liquids and number of drops the surface tension γ_2 of unkown liquid can be calculated.

3. Torsion method by Tensiometer: A plate a platinum ring can be used, which is submerged in the liquid. The amount of torsion produced in the ring wires gives a measure of force that is used in detaching the ring from the surface of the liquid (the torsion is given by angle).



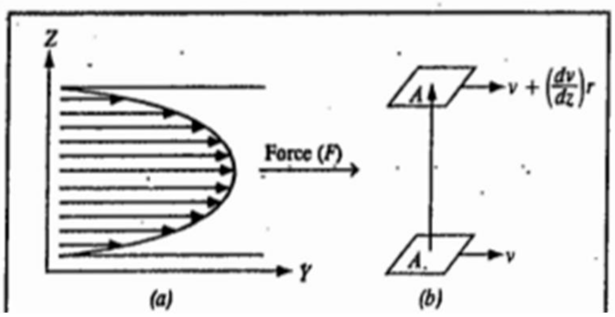
If the torsion angle is θ_1 for one liquid and θ_2 for the second liquid, then

θ_1 α $F_1 = 2x2\pi r\gamma_1$ and θ_2 α $F_2 = 2x2\pi r\gamma_2$ (the surface tension multiplied by 2 because it acts on the two circumference of the ring i.e. inside and outside the ring)

Hence, $\frac{\theta 1}{\theta 2} = \frac{\gamma 1}{\gamma 2}$ Where γ_1 and γ_2 are surface tensions of two liquids. If surface tension of one of the liquid (standard) is known then that of the other can be easily calculated.

Viscosity

Viscosity may be defined as the force of friction between two layers of a liquid moving past one another with different velocities.



The velocity profile during flow of a liquid in a glass tube.

Consider the laminar flow of liquid in y direction. The layer in contact with the wall of the tube is stationary. However, the velocity of the successive layers increases as move away from the surface. If the distance between two layers is r and v is the velocity of slow moving layer. As a result velocity gradient is set up along z-direction.

If we want to maintain the velocity gradient, we must apply an external force along y-axis. This force (F) is proportional to common area of two layers (A) and velocity gradient.

$$F \propto A(dv/dz) = -\eta A(dv/dz)$$

Where the proportionality constant η is coefficient of viscosity, $\frac{dv}{dz}$ is velocity gradient. The minus sign shows that the viscous force on faster layer is in opposite direction to its motion. The reciprocal of viscosity is called **fluidity**. It is denoted by $\varphi = 1/\eta$

Coefficient of viscosity (η): If A = 1 cm^2, dv = 1 cm/s, dz =1 cm, then **F = η,** Coefficient of viscosity of a fluid is defined as the tangential force per unit area which is required to maintain a unit velocity gradient between its layers.

Unit: The SI unit of viscosity is the pascal-second (Pa·s), or equivalently kilogram per meter per second ($kg \cdot m^{-1} \cdot s^{-1}$). The CGS unit is the poise (P, or $g \cdot cm^{-1} \cdot s^{-1} = 0.1$ Pa·s).

Effect of Temperature on Viscosity of Liquid:

The relationship between the coefficient of viscosity and temperature is expressed as:

$$\boldsymbol{\eta = Ae^{Ea/RT}}$$

Where A is constant. Ea is called the activation energy for viscous flow. From the equation it is clear that the viscosity decreases with increase of temperature. Viscosity in liquid is mainly due to the cohesive force (inter molecular force of attraction). Increase in the temperature reduces the cohesive forces between the molecules of liquid and hence the viscosity decreases.

In contrast to liquid the viscosity of gases increases with increasing temperature.

Determination of Viscosity by Ostwald Viscometer: This method is based on Poiseuille's law. The rate of flow of a liquid through a capillary tube with the coefficient of viscosity of the liquid is expressed by the equation:

$\eta = (\pi r^4 tP)/8Vl$ ....*(1)*

Where V is the volume in ml of the liquid flowing in t seconds through a narrow tube of radius r cm and length l cm under hydrostatic pressure P dynes per square centimeter and η is coefficient of viscosity in poises.

since, $P = h\rho g$ *----(2)*

Then equation (1) becomes:

$\eta = (\pi r^4 th\rho g)/8Vl$ ....*(3)*

The fixed volume of liquid is filled in bulb A and sucked and then allowed to flow between the mark C and D.

For liquid 1: $\eta_1 = (\pi r^4 t_1 h\rho_1 g)/8Vl$ -----*(4)*

For liquid 2: $\eta_2 = (\pi r^4 t_2 h\rho_2 g)/8Vl$ -----*(5)*

The value of h is same in both cases since equal volume of both liquids are taken.

OSTWLAD VISCOMETER:- I

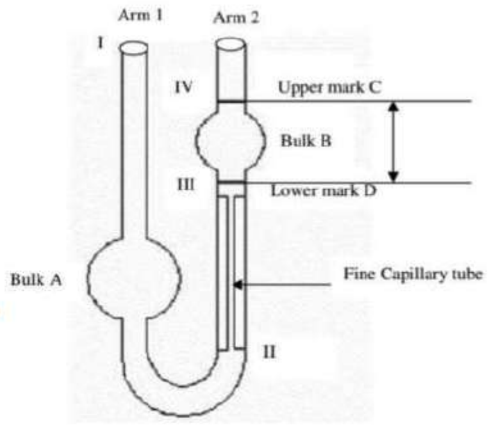


Fig. 1:- Ostwald Viscometer

Hence,

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

Liquid 1 taken as water, by knowing the *coefficient of viscosity of water (η_1) that of other liquid (η_2), can easily be calculated.*

Question: Benzene takes 46 s to flow through an viscometer while water takes 68 s, at the same temperature. The respective densities are 0.8 and 0.998 g/cm^3. Coefficient of viscosity of water is 1.008 centipoise. Calculate coefficient of viscosity of benzene.

Answer: Let η_1, η_2 coefficient of viscosity of benzene and water, respectively

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \text{ or, } \eta_1 = \frac{\eta_2 \rho_1 t_1}{\rho_2 t_2} = \frac{(1.008\ x\ 10^{-2} dynecm^{-2} s)(0.8 gcm^{-3})(46s)}{(0.998\ gcm^{-3})(68s)}$$

= 0.0065 dynecm^{-2}s = 0.0065 poise = 0.65 centipoise