02 States of Matter and Eudiometry

Ideal Gas

Introduction :

Matter, as we know, broadly exist in three states - solid, liquid and gas.

There are always two opposite tendencies between particles of matter which determine the state of matter :

- Intermolecular forces.
- The molecular motion / random motion (energy of particles)

Intermolecular forces are the forces of attraction and repulsion between atoms or molecules. Attractive intermolecular forces are known as ***Vander Waals forces***. These are dispersion forces, dipole-dipole forces & dipole induced forces. When two molecules are brought very close, they will exert repulsive forces. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason that liquid & solids are hard to compress. In these states, molecules are already in close contact, therefore they resist further compression (in that case repulsive interaction will increase)

Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles. This movement of particles is called ***thermal motion***. Intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

General characteristics of solid, liquid & gas :

Each physical state of matter possesses characteristics properties of its own. For example,

Solids :

All solids show the following characteristics :

(i) Solids are rigid and incompressible.

(ii) Solids have fixed shape and definite volume.

(iii) Solids have their melting and boiling points above room temperature.

(iv) Density of solid is high.

Liquids :

All liquids show the following characteristics :

(i) Liquids are almost incompressible but less incompressible than solids.

(ii) Liquids have fixed volume but no fixed shape.

(iii) Liquids have their melting points below room temperature and boiling points above room temperature, under normal conditions.

(iv) Density of liquids is lower than that of solids but much higher than that of gases.

Gases :

All gases show the following characteristics :

(i) Gases are highly compressible, i.e. gases can be compressed easily by applying pressure.

(ii) Gases have no fixed volume and shape. Gases fill the container of any size and shape completely.

(iii) Gases can diffuse into each other rapidly.
(iv) Gases have their melting and boiling points both below room temperature.
(v) Gases generally have low density.

Measurable Properties of Gases

The characteristics of gases are described fully in terms of four parameters or measurable properties :
(I) Amount of the gas (i.e., mass or number of moles).
(II) Volume (V) of the gas.
(III) Temperature (T)
(IV) Pressure (P)

I. Amount of the gas :

(i) The mass of a gas can be determined by weighing the container in which the gas is enclosed and again weighing the container after removing the gas. The difference between the two masses gives the mass of the gas.
Mass of gas (m) = Mass of filled container – mass of empty container
(ii) The mass of the gas is related to the number of moles of the gas as
Moles of gas (n) = Mass in grams / Molar mass = m/M
(iii) Mass is expressed in gram or kg.

II. Gas volume :

(i) Since gases occupy the entire space available to them, the measurement of volume of a gas only requires a measurement of the container confining the gas.
(ii) Volume is expressed in litres (L), millilitres (mL) or cubic centimetres (cm^3) or cubic meters (m^3).
(iii) 1 L = 1000 mL; 1 L = 1 dm^3 = 10^{-3} m^3
1 m^3 = 10^3 dm^3 = 10^6 cm^3 = 10^6 mL = 10^3 L
1 mL or 1 cc = 1 cm^3

III. Temperature :

(i) Gases expand on increasing the temperature.
(ii) Temperature is measured in degree centigrade (°C) or Celsius degree with the help of thermometers. Temperature is also measured in degree Fahrenheit (°F).
(iii) S.I. unit of temperature is kelvin (K) or absolute degree
K = °C + 273
(iv) Relation between °F and °C is
°C/5 = (°F – 32) / 9

IV. Pressure :

Force exerted by the gas per unit area of the walls of the container in all directions. Thus,
Pressure (P) = Force(F) / Area(A)
Atmospheric pressure :
The pressure exerted by atmosphere on earth's surface at sea level is called atmospheric pressure. Generally, its unit is atm.
Pressure(P) = Force(F) / Area(A)
= Mass(m) × Acceleration(g) / Area(a)
= Volume × density × Acceleration(g) / Area(a)
= Area (a) × height (h) × density (ρ) × Acceleration(g) / Area(a)
Pressure(P) = hρg
where h = Height of mercury column in the barometer.
ρ = Density of mercury.
g = Acceleration due to gravity.

Pressure does not depend on the cross section of tube, but only on the vertical height of the Hg. If area is doubled, volume also gets doubled and mass will also get doubled. Now it will rest on twice area but pressure exerted remains same.

1 atm = 1.013 bar = 1.013×10^5 N/m^2 = 1.013×10^5 Pa

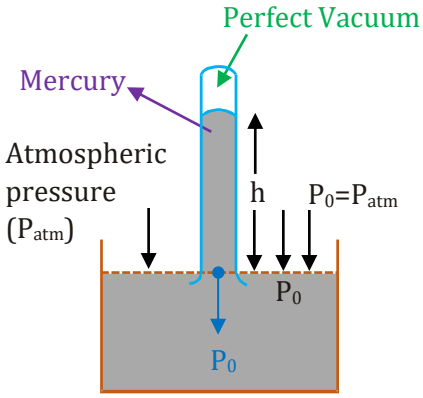
1 atm = 76 cm of Hg = 760 mm of Hg = 760 torr

Pressure Measuring Devices

Generally, the instruments used for the calculation of pressure of a gas are ***barometer*** and ***manometer***.

(i) Barometer :

A barometer is an instrument that is used for the measurement of atmospheric pressure. The construction of the barometer is as follows -



A thin narrow calibrated capillary tube is filled up to the brim, with a liquid such as mercury, and is inverted into a trough filled with the same fluid. Now depending on the external atmospheric pressure, the level of the mercury inside the tube will adjust itself, the reading of which can be monitored. When the mercury column inside the capillary comes to rest, then the net forces on the column should be balanced.

$\Rightarrow$ $P_0 \times A = \rho A \times gh$

$\Rightarrow$ $\boxed{P_0 = \rho gh}$; where ρ is the density of the fluid.

(ii) Manometer :

(a) Open end manometer :

It consists of a U-shaped tube partially filled with mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel containing the gas whereas the longer limb is open as shown in fig. The mercury in the longer tube is subjected to the atmospheric pressure while mercury in the shorter tube is subjected to the pressure of the gas.

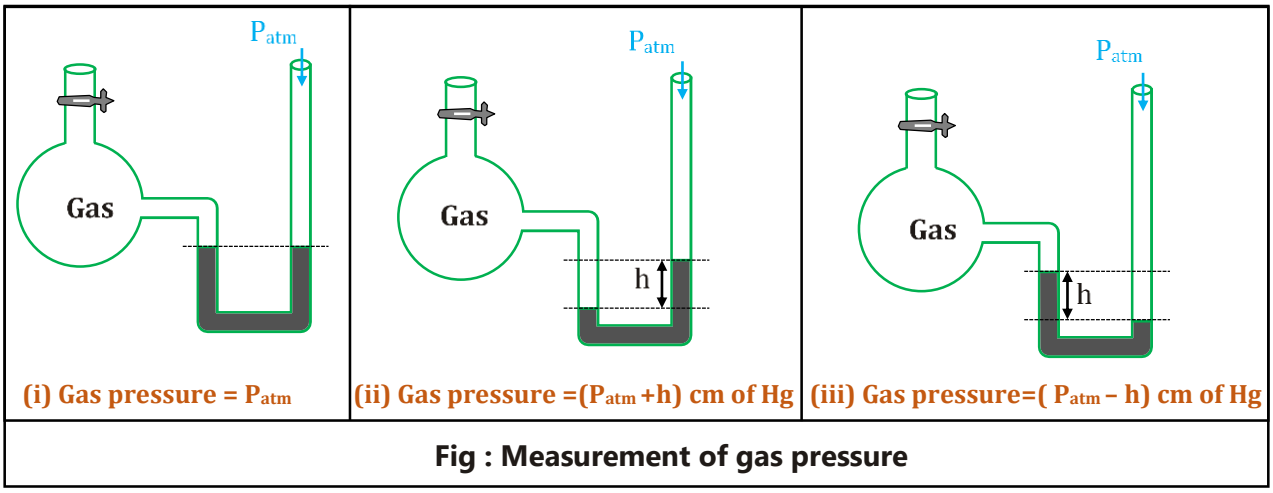
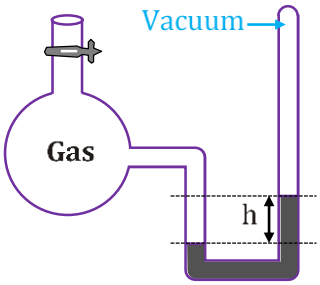


Fig : Measurement of gas pressure

Where P_{atm} = 76 cm of Hg and h = Height in cm of Hg
There are three possibilities as described below :
(i) If the level of Hg in the two limbs is same, then gas pressure = atmospheric pressure (P_{atm}).
(ii) If the level of Hg in the longer limbs is higher, gas pressure
= P_{atm} + (difference between the two levels)
= P_{atm} + h.
(iii) If the level of Hg in the shorter limb is higher, then gas pressure
= P_{atm} – (difference between the two levels)
= P_{atm} – h.

(b) Closed end manometer :

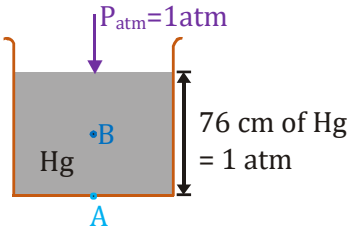
This is generally used to measure low gas pressure.
It also consists of U-tube with one limb shorter than the other and partially filled with mercury as shown in fig. The space above mercury on the closed end is completely evacuated. The shorter limb is connected to the vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.
Gas pressure = [Difference in the Hg level in two limbs]



Closed end manometer

Illustration 1:
Why mercury is used in the barometer tube?
Solution:
Mercury, a liquid with very high density, is normally used in the barometer because it does not stick to the surface of the glass tube. Mercury is also non-volatile at room temperature. Therefore, there are hardly any vapours of mercury above the liquid column and their pressure, if any, can be neglected. Due to high density of mercury, height of mercury column will be small and can be easily measured.

Illustration 2:
An open tank is filled with Hg upto a height of 76cm.
Find the pressure at the
(a) Bottom (A) of the tank
(b) Middle (B) of the tank.
(If atmospheric pressure is 1 atm)

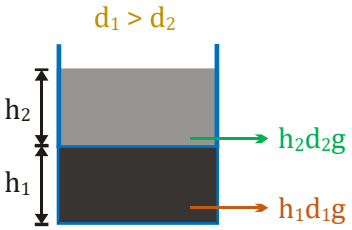


Solution:
(a) At bottom,
$P_A = P_{atm} + P_{Hg}$
= 1 + 1 = 2 atm
(b) At middle,
$P_B = P_{atm} + P_{Hg}$
= 1 + ½ = 1.5 atm

Illustration 3:
Find the height of water upto which water must be filled to create the same pressure at the bottom, as in above problem.
Given that $d_w = 1\ gm/cm^3$, $d_{Hg} = 13.6\ gm/cm^3$, $h_{Hg} = 76$ cm
Solution:
$P_{water} = P_{Hg}$
$h_w d_w g = h_{Hg} d_{Hg} g$
$h_w d_w = h_{Hg} d_{Hg}$
$h_w \times 1\ g/cm^3 = 76\ cm \times 13.6\ g/cm^3$
$h_w = 1033.6$ cm

Illustration 4:

What will be the pressure if two immiscible fluid is filled according to given diagram.



(a) Find the pressure at the bottom of tank.

(b) Find the pressure at the middle point of bottom layer.

Solution:

(a) $P_{atm} + h_2d_2g + h_1d_1g$;

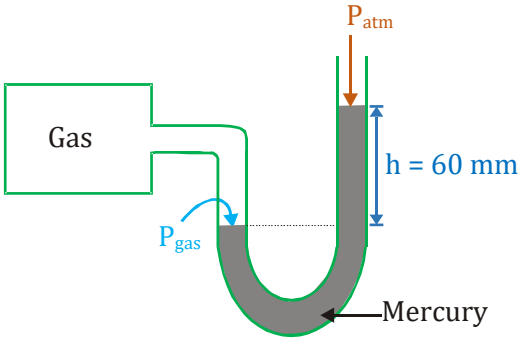
(b) $P_{atm} + h_2d_2g + \frac{h_1}{2} d_1g$

Illustration 5:

Find the pressure of the gas inside a container if the open manometer attached to the container shows a difference of 60 mm.

Solution:

Case-I : $P_{atm} < P_{gas}$

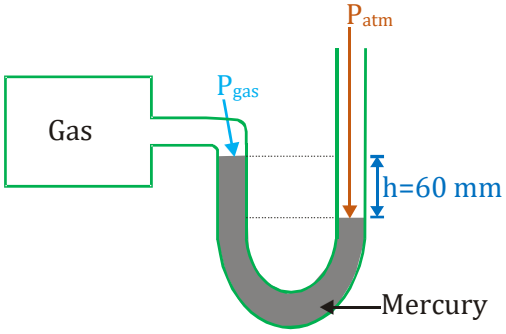


$P_{gas} = P_{atm} + 60$ mm

$= 760$ mm $+ 60$ mm

$= 820$ mm of Hg

Case-II : $P_{atm} > P_{gas}$



$P_{atm} = P_{gas} + 60$ mm

760 mm $= P_{gas} + 60$

$P_{gas} = 700$ mm

Gas Laws

The behaviour of the gases is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas.

The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as ***Boyle's Law***. Later on, attempts to fly in air with the help of hot air balloons motivated Jacques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from *Avogadro* and others provided lot of information about gaseous state.

1. Boyle's Law :

For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or pressure of the gas.

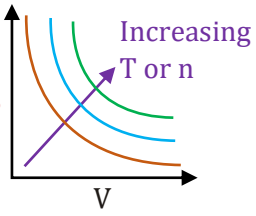
$\Rightarrow V \alpha \frac{1}{P}$

$\Rightarrow$ Hence, PV = const. (K)

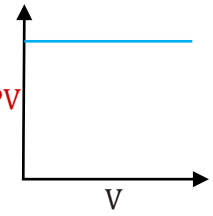
$\Rightarrow \boxed{P_1V_1 = P_2V_2}$

Graphical representation of Boyle's law :

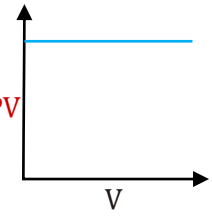
(i) P v/s V :



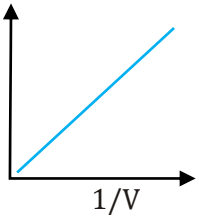
(ii) PV v/s V :



(iii) PV v/s P :



(iv) P v/s 1/V :



2. Charle's Law :

For a fixed amount of gas at constant pressure, volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$\Rightarrow V \alpha T$

$\Rightarrow V = KT$

$$\boxed{\frac{V}{T} = \text{constant } (K)}$$

T = Temperature on absolute scale, kelvin scale or ideal gas scale.

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

$$\boxed{V = V_0 + bt}$$

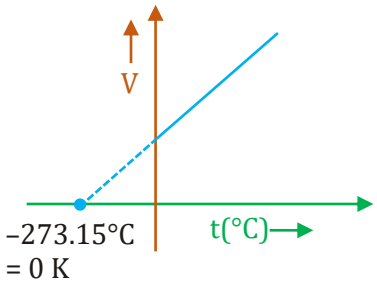
t = temperature on centigrade scale.
V_0 = volume of gas at 0°C.

$$\boxed{V = b'T}$$

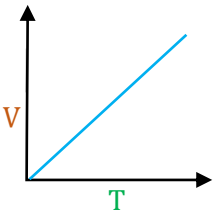
T = absolute temperature (K)
b, b' = constants

Graphical representation of Charle's Law :

(i) V v/s t (°C) :



(ii) V v/s T :

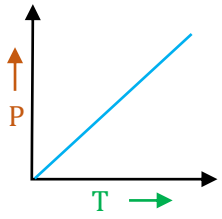


Important Points :

- Since volume is proportional to absolute temperature, the volume of a gas should be theoretically zero at absolute zero temperature.
- In fact, no substance exists as gas at a temperature near absolute zero, though the straight-line plots can be interpolated to zero volume. Absolute zero can never be attained practically though it can be approached only.
- By considering –273.15°C as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

Gay-Lussac's law :

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.



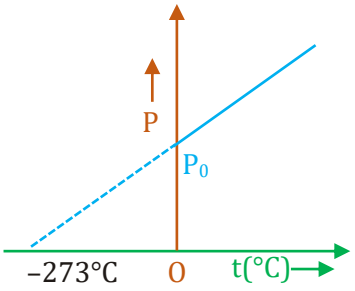
$\Rightarrow$ $P \propto T$

$\frac{P}{T}$ = constant (K)

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$ Temperature on absolute scale, kelvin scale or ideal gas scale.

Note :

Originally, the law was developed on the centigrade scale, where it was found that pressure is a linear function of temperature $\Rightarrow$ $\boxed{P = P_0 + bt}$,



where 'b' is a constant and 'P_0' is pressure at zero degree centigrade.

But for kelvin scale : $\boxed{P = b"T}$ where T is in K.

Avogadro's law :

Equal volumes of all the gases under similar conditions of temperature and pressure contains equal number of molecules or moles of molecules (not atoms).

$V \propto N$ (Temperature and pressure constant)

$V \propto n$ (Temperature and pressure constant)

Where, N = number of molecules, n = number of moles of molecules

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2} \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP) will have same volume.

Standard temperature and pressure mean 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure. At STP, molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol^{-1}.

Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).

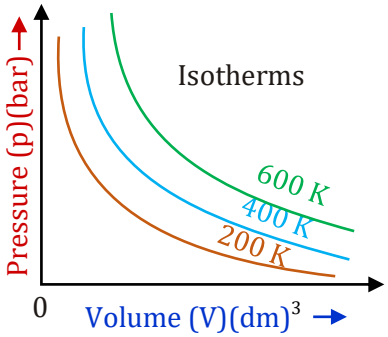
Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

Illustration 6:

What is a pressure-volume isotherm ?

Solution:

Graph between P & V at constant temperature is called ***PV-isotherm***.



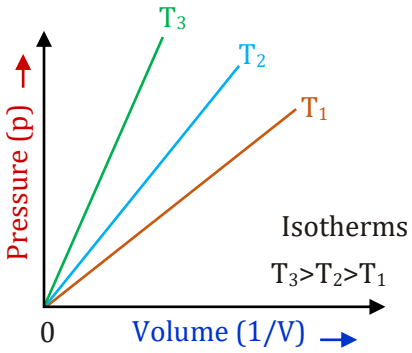


Illustration 7:

What is Isobar ?

Solution:

Graph plotted at constant pressure is called isobar. Graph between V & T at constant pressure is called VT-isobar.

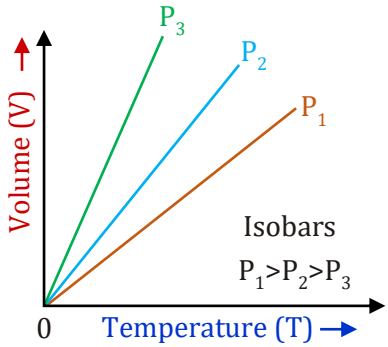
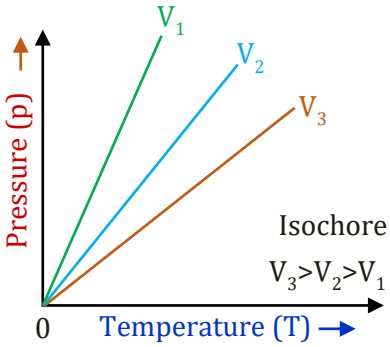


Illustration 8:

What is Isochore ?

Solution:

Graph plotted at constant volume is called isochore. Graph between P & T at constant volume is called PT-isochore.



Ideal Gas Equation

A single equation which is combination of Boyle's, Charle's & Avogadro's Law is known as ***Ideal gas equation***. Or we can say a single equation which describe the simultaneous effects of the change in temperature & pressure on volume of the given amount of the gas is called the ***Ideal gas equation.***

$PV = nRT$

According to Boyle's law, $V \propto \frac{1}{P}$ (at constant T and n)

According to Charle's law, $V \propto T$ (at constant P and n)

According to Avogadro's law, $V \propto n$ (at constant T and P)

According to the three laws, $V \propto \frac{nT}{P}$ or $PV \propto nT$

or $PV = nRT$ [Equation of state or combined gas law]

Where R is a constant called ***Universal gas constant,*** which does not depend on variables (P, V, n, T) and nature of gas.

Molar volume is the volume of 1 mole of gas.

$$\text{Molar volume } (V_m) = \frac{\text{Volume}}{\text{mole}}$$

$PV_m = RT$

Volume of 1 mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.7 L mol^{-1}.

Dimension of R :

$$R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Mole} \times \text{Temperature}} = \frac{(\text{Force}/\text{Area}) \times (\text{Area} \times \text{Length})}{\text{Mole} \times \text{Temperature(K)}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Temperature(K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Temperature(K)}}$$

Physical significance of R :

The dimensions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1 K isobarically.

Units of R :

(i) In lit-atm $R = \frac{1\,\text{atm} \times 22.4\,\text{lit.}}{1\,\text{mol} \times 273\ \text{K}}$ **= 0.0821 lit-atm $mol^{-1}K^{-1}$**

(ii) In C.G.S system $R = \frac{1 \times 76 \times 13.6 \times 980\ \text{dyne cm}^{-2} \times 22400\,\text{cm}^3}{1\,\text{mol} \times 273\ \text{K}}$

= 8.314 × 10^7 erg $mole^{-1}$ K^{-1}.

(iii) In M.K.S. system (SI units) R **= 8.314 Joule $mole^{-1}$ K^{-1}.** [10^7 erg = 1 joule]

(iv) In calories, $R = \frac{8.314 \times 10^7\ \text{erg mole}^{-1}\text{K}^{-1}}{4.184 \times 10^7\ \text{erg}}$

$= 1.987 \approx$ **2 calorie mol^{-1} K^{-1}.**

Illustration 9:

A sample of gas occupies 100 dm^3 at 1 bar pressure and at T °C. If the volume of the gas is reduced to 5 dm^3 at the same temperature, what additional pressure must be applied ?

Solution:

From the given data :

$P_1 = 1$ bar $P_2 = ?$

$V_1 = 100\ dm^3$ $V_2 = 5\ dm^3$

Since the temperature is constant, Boyle's law can be applied

$$P_1V_1 = P_2V_2 = P_2 = \frac{P_1V_1}{V_2}$$

$$P_2 = \frac{(1\,bar)\times(100\,dm^3)}{(5\,dm^3)} = 20\,bar$$

$\therefore$ Additional pressure applied = 20 – 1 = 19 bar

Illustration 10:

A certain amount of a gas at 27°C and 1 bar pressure occupies a volume of 25 m^3. If the pressure is kept constant and the temperature is raised to 77°C, what will be the volume of the gas ?

Solution:

From the available data :

$V_1 = 25\ m^3$ $\quad$ $T_1 = 27 + 273 = 300\ K$

$V_2 = ?$ $\quad$ $T_2 = 77 + 273 = 350\ K$

Since the pressure of the gas is constant, Charles law is applicable

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

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

$$V_2 = \frac{(25\,m^3)\times(350\,K)}{(300\,K)} = 29.17\ m^3$$

Illustration 11:

The density of a gas is found to be 1.56 g dm^{-3} at 0.98 bar pressure and 65°C. Calculate the molar mass of the gas.

Use R = 0.083 dm^3 bar K^{-1} mol^{-1}

Solution:

We know that :

$$M = \frac{dRT}{P} = \frac{(1.56\,g\,dm^{-3})\times(0.083\,dm^3\,bar\,K^{-1}\,mol^{-1})\times 338K}{(0.98\,bar)} = \mathbf{44.66\ g\ mol^{-1}}$$

Illustration 12:

A glass bulb of 2 L capacity is filled by helium gas at 10 atm pressure. Due to a leakage the gas leaks out. What is the volume of gas leaked if the final pressure in container is 1 atm.

Solution:

$P_1 \times 2\ L = P_2 \times V$

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

$\Rightarrow$ $20 = V$

$V = V' + 2\ L$

$20 = V' + 2\ L$

V' **= 18 L**

$\Rightarrow$ total volume of gas leaked

Illustration 13:

LPG is a mixture of n-butane & iso-butane. What is the volume of oxygen needed to burn 1 kg of LPG at 1 atm, 273 K ?

Solution:

During the burning of LPG following reaction takes place -

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$$

Now, for complete combustion of 1 mole of LPG $\longrightarrow \frac{13}{2}$ moles of O_2 are required.

$\therefore$ for $\frac{1000}{58}$ moles of LPG $\longrightarrow \frac{13}{2}\times\frac{1000}{58}$ moles of O_2 are required.

Thus, the volume of oxygen needed to burn 1 kg of LPG at 1 atm & 273K would be

Vol. of O_2 = Moles of $O_2 \times 22.4$ L = $\frac{13}{2}\times\frac{1000}{58}\times 22.4$ = **2510 L**

Illustration 14:

The best vacuum so far attained in laboratory is 10^{-10} mm of Hg. What is the number of molecules of gas remain per cm^3 at 20°C in this vacuum ?

Solution:

Given conditions -

$P = 10^{-10}$ mmHg = $\frac{10^{-10}}{760}$ atm; $V = 1\ cm^3 = \frac{1}{1000}$ L; $T = 20°C = 293$ K

No. of molecules, N = ?

Now, applying

$PV = nRT$

$\therefore$ number of molecules per cm^3, $N = \frac{N_A \times P \times V}{RT}$

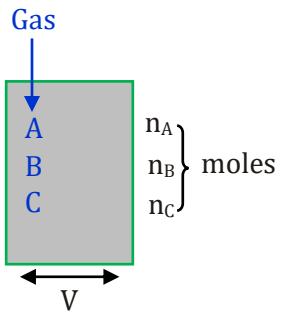
$\Rightarrow N = \frac{6.023 \times 10^{23} \times (10^{-10}/760)\times(1/1000)}{(0.0821)(293)}$

$N = 3.29 \times 10^6$ molecules

Dalton's Law of Partial Pressures

Partial pressure :

In a mixture of non-reacting gases, partial pressure of any component gas is defined as the pressure exerted by the individual gas if whole of the volume of mixture had been occupied by this component only.



Partial pressure of component gases are -

$P_A = \frac{n_A RT}{V}$ = partial pressure of A

$P_B = \frac{n_B RT}{V}$ = partial pressure of B

$P_C = \frac{n_C RT}{V}$ = partial pressure of C

Dalton's Law :

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases."

$P_{Total} = p_1 + p_2 + p_3 + ...$ (At constant V and T)

$= \left(\frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + ...\right) RT = (n_1 + n_2 + n_3 + ...)\ \frac{RT}{V} = \frac{nRT}{V}$

Where $n = n_1 + n_2 + n_3 + ... =$ Total moles, V = Total volume

$$P_{Total} = \Sigma p_i = \frac{RT}{V}\Sigma n_i$$

Dalton's law of partial pressure is applicable only to non-reacting gases.

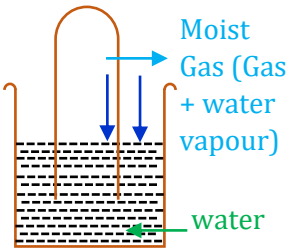
If the two non-reacting gases A and B having n_A and n_B number of moles respectively are filled in a vessel of volume V at temperature T, then

$$\frac{p_A}{P} = \frac{n_A RT/V}{(n_A + n_B)RT/V} = \frac{n_A}{n_A + n_B} = x_A \text{ (mole fraction of A)}$$

$p_A = x_A \times P$, Similarly $p_B = x_B \times P$

Partial pressure of a component = Mole fraction × total pressure.

It has been observed that gases are generally collected over water and therefore are moist.



$$P_{dry\ gas} = P_{moist\ gas} - P_{water\ vapour}$$

or Pressure of dry gas = Pressure of moist gas – aqueous tension

The pressure exerted by water vapour is constant when it is in equilibrium with liquid water at a particular temperature. It is called vapour pressure of water or ***aqueous tension***, which varies with the temperature and becomes 760 mm at 100°C.

$$\text{Relative Humidity (RH)} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water (aq.tension)}}$$

Amagat's Law of Partial Volume

Partial Volume :

Partial volume of any component is defined as the volume occupied by that particular component when it is kept at same total pressure and temperature as of the mixture.

Amagat's law :

According to this law at constant temperature and pressure, the total volume of mixture of non-reacting gases is equal to the sum of partial volumes of each component present in mixture.

$$V_T = V_1 + V_2 + V_3 + ...$$

Let us consider three non-reacting gases A, B and C are present in a container which have no. of moles n_A, n_B and n_C respectively. For each gas partial volume is

$$V_A = n_A\left(\frac{RT}{P}\right) = \text{partial volume of A}$$

$$V_B = n_B\left(\frac{RT}{P}\right) = \text{partial volume of B}$$

$$V_C = n_C\left(\frac{RT}{P}\right) = \text{partial volume of C}$$

Total volume :

$$V_T = V_A + V_B + V_C = (n_A + n_B + n_C)\left(\frac{RT}{P}\right) = n_T\left(\frac{RT}{P}\right)$$

$$\frac{V_A}{V_T} = \frac{n_A}{n_T} = x_A \quad \text{(Mole fraction of gas A)}$$

$\frac{V_B}{V_T} = \frac{n_B}{n_T} = x_B$ (Mole fraction of gas B)

$\frac{V_C}{V_T} = \frac{n_C}{n_T} = x_C$ (Mole fraction of gas C)

$\therefore$ **Partial volume of a gas = Mole fraction × Total volume**

Illustration 15:

(a) Find the total pressure and partial pressure of each component if a container of volume 8.21 lit. contains 2 moles of A and 3 mole of B at 300K.

(b) What will be the final pressure and partial pressure of each component if 5 moles of C is also added to the container at same temperature.

Solution:

(a) $P_A = \frac{n_A RT}{V} = \frac{2 \times 0.0821 \times 300}{8.21} = 6$ atm

$P_B = \frac{n_B RT}{V} = \frac{3 \times 0.0821 \times 300}{8.21} = 9$ atm

Total pressure $P_T = P_A + P_B = 6 + 9 = 15$ atm

(b) $P_C = \frac{n_C RT}{V} = \frac{5 \times 0.0821 \times 300}{8.21} = 15$ atm

Note :

If we add or remove a non-reacting gas partial pressure of other gases remains unchanged.

$P_T = P_A + P_B + P_C = 6 + 9 + 15 = 30$ atm

Illustration 16:

2 moles of $NH_3(g)$ and 1 mole of HCl(g) are taken in a container of capacity 8.21 lit at 300K to produce $NH_4Cl(s)$. Find the total pressure after the reaction.

Solution:

	$NH_3(g)$ +	$HCl(g) \longrightarrow$	$NH_4Cl(s)$
initial	2	1	
after reaction	1	0	

In this reaction HCl is L.R. so it will be completely consumed. We don't consider pressure due to solid.

$\therefore$ $P_T = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{8.21} = 3$ atm

Illustration 17:

A closed container containing O_2 and some liquid water was found to exert 740 mm pressure at 27°C.

(a) Then calculate the pressure exerted by O_2 if aqueous tension at 27°C is 20 mm.

(b) What will be the final pressure if volume is reduced to half.
(consider volume of liquid water negligible)

(c) What will be the final pressure if volume is doubled.

Solution:

(a) $P_T = P_{\text{dry gas}} + P_{\text{aq. tension}}$

$740 = P_{O_2} + 20 = 740 - 20 = 720$ mm

(b) $\left(P_{O_2}V_{O_2}\right)_{initial} = \left(P_{O_2}V_{O_2}\right)_{final}$ (Boyle's law)

$720 \times V = P_{O_2} \times \frac{V}{2}$

$P_{O_2} = 1440$ mm

$P_T = P_{O_2} + P_{aq.} = 1440 + 20 = 1460$ mm

(c) $\left(P_{O_2}V_{O_2}\right)_{initial} = \left(P_{O_2}V_{O_2}\right)_{final}$

$720 \times V = P_{O_2} \times 2V$

$P_{O_2} = 360$ mm

$P_T = P_{O_2} + P_{aq.} = 360 + 20 = 380$ mm

Problem Related with Different Type of Containers

I. Closed Container :

In this case gas can neither go outside nor it can come inside. So, number of moles of gas is always constant. Closed container can be of following types -

(a) Closed rigid container : In this case number of moles constant, volume constant.

At this condition :

Initial Final

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

Example : Gas cylinder

(b) Closed non rigid container : (fitted with freely movable piston)

In this kind of container inside pressure is always equal to outside pressure, i.e., atmospheric pressure so that n = constant, p = constant

Ex: Balloon, Water bubble

Initial Final

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

Illustration 18:

A balloon is inflated to $\frac{7}{8}$ of its maximum volume at 27°C then calculate the minimum temperature above which it will burst.

Solution:

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

$\frac{7V}{8 \times 300} = \frac{V}{T}$

T = 342.8 K

Illustration 19:

A gas cylinder containing cooking gas can with stand a pressure of 18 atm. The pressure gauge of cylinder indicates 12 atm at 27°C. Due to sudden fire in building the temperature start rising at what temperature will the cylinder explode.

Solution:

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

$$\frac{12}{300}=\frac{18}{T}$$

T = 450 K

II. Tyre tube type container :

In this case temperature is always constant. Initially on adding gas volume of tube will increase and pressure of tube will remain constant until it will gain maximum volume.

$\because$ $V \propto n$

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

After attaining maximum volume on adding gas pressure reach to a maximum possible pressure. Hence at this condition volume constant or temperature constant.

V = constant T = constant

$P \propto n$

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

Illustration 20:

A tyre tube of maximum volume 8.21 lit. can withstand a pressure of 10 atm. Initially the tube is empty.

(i) Calculate the number of moles required to inflate completely the tube upto a pressure of 1 atm & 300 K temperature.

(ii) Calculate the minimum number of moles required to burst the tyre tube at 300 K.

Solution:

(i) PV = nRT

$1 \times 8.21 = n_1 \times 0.0821 \times 300$

$n_1 = \frac{1}{3}$

(ii) PV = nRT

$10 \times 8.21 = n_2 \times 0.0821 \times 300$

$n_2 = \frac{10}{3}$

III. Open rigid container :

When air is heated in an open vessel, pressure is always atmospheric pressure i.e., constant and volume is also constant.

At this condition

Initial Final

$n_1 T_1 = n_2 T_2$

n_1 = initial number of moles

n_2 = final number of moles

$\mathbf{n_{initial} = n_{final} + n_{removed}}$.

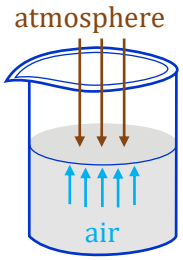


Illustration 21:

An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that

(a) 1/3rd of air measured in the container at 27°C escape out.

(b) 1/3rd of air measured in the container at final temperature escape out.

Solution:

(a) $\mathbf{n_{initial} - n_{final} = n_{expelled}}$

$$\frac{PV}{R\times 300}-\frac{PV}{R\times T}=\frac{1}{3}\times\frac{PV}{R\times 300}=\frac{1}{300}-\frac{1}{T}=\frac{1}{900}$$

$$\frac{1}{T}=\frac{1}{300}-\frac{1}{900}=\frac{3-1}{900}=\frac{2}{900} \Rightarrow T = 450\ K = 177°C$$

(b) $\mathbf{n_{initial} - n_{final} = n_{expelled}}$

$$\frac{PV}{R\times 300}-\frac{PV}{R\times T}=\frac{1}{3}\times\frac{PV}{R\times T}$$

$$\frac{1}{300}-\frac{1}{T}=\frac{1}{3\times T}$$

$\Rightarrow$ T = 400 K = 127°C

Illustration 22:

A bulb of unknown volume containing air is heated from 27°C to 227°C at constant pressure. The expelled air is measured at different temperature of determine volume of container. What will be volume of container if -

(a) 200 ml of air measured at 227°C was expelled.

(b) 200 ml of air measured at 27°C was expelled.

(c) 200 ml of air measured at 127°C was expelled.

Solution:

(a) $\mathbf{n_{initial} - n_{final} = n_{expelled}}$

$$\frac{PV}{R\times 300}-\frac{PV}{R\times 500}=\frac{P\times 200}{R\times 500}$$

$$\frac{V}{3}-\frac{V}{5}=\frac{200}{5}$$

$$\frac{5V-3V}{15}=\frac{200}{5} \quad \Rightarrow \quad 2V=\frac{200\times 15}{5} \Rightarrow V = 300\ ml$$

(b) $$\frac{PV}{R\times 300}-\frac{PV}{R\times 500}=\frac{P\times 200}{R\times 300}=\frac{2V}{15}=\frac{200}{3} \Rightarrow V=\frac{100\times 15}{2\times 3}=500\ ml$$

(c) $$\frac{PV}{R\times 300}-\frac{PV}{R\times 500}=\frac{P\times 200}{R\times 400}$$

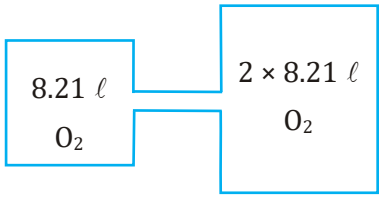
$$\frac{2V}{15}=\frac{200}{4} \Rightarrow V=\frac{200\times 15}{2\times 4}=375\ ml$$

IV. Connected Container :

If containers are connected for substantial time then gases move from one container to another container till partial pressure of each component of mixtures becomes equal in all connected containers (irrespective whether containers have same or different temperature and volumes)

Illustration 23:

A container of 8.21 lit. capacity is filled with 1 mole of H_2 at 300 K and it is connected to another container of capacity 2 × 8.21 lit. containing 4 moles of O_2 at 300 K, then find the final pressure & partial pressure of each gas.



Solution:

$P_fV_f = n_fRT$

$P_f(3 \times 8.21) = 5 \times 0.0821 \times 300$

$P_f = 5$ atm

$P_{H_2} = x_{H_2}$, $P_f = \frac{1}{1+4} \times 5 = 1$ atm

$P_{O_2} = x_{O_2}$, $P_f = \frac{4}{1+4} \times 5 = 4$ atm

Illustration 24:

A 10 litre container consist of 1 mole of gas at 300 K. It is connected to another container having volume 40 litre and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate

(a) Moles and pressure of gas in both the containers before heating.

(b) Moles and pressure in two containers after heating.

(Assume that initially the larger container is completely evacuated.)

Solution:

(a) Before heating :

$P_I = P_{II}$

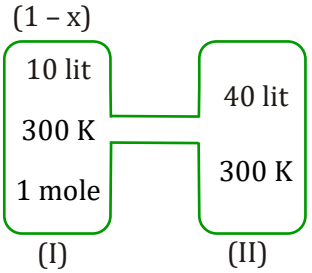
$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$

$x = 0.8$ moles

$n_I = 1 - x = 0.2$ mole

$n_{II} = x = 0.8$ mole

Pressure $= \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492$ atm



(b) After heating :

$\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$

$x_1 = 0.67$ moles, Given $T_1 = 600$ K

Pressure $= \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times .0821 \times 600}{40} = 0.821$ atm

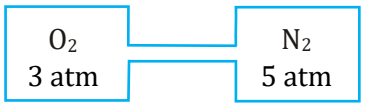
Graham's Law of Diffusion & Effusion

Diffusion :

The ***diffusion*** is the process of gradual mixing of molecules of one gas with molecules of another gas due to their molecular motion (kinetic energy). The diffusion always proceeds from a region of high concentration to a region of lower concentration (or high partial pressure to low partial pressure). For example, when a bottle of perfume is opened at one end of the room, the person sitting at the other end of the room can smell the perfume because of the diffusion process of perfume molecules.

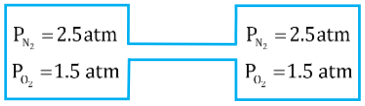
Note :

Initially



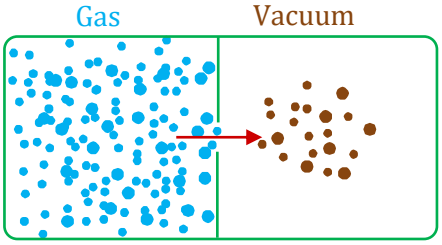
When stop cock is removed flow will be from both sides, N_2 will try to equalise its partial pressure in both the vessels, and so will O_2.

Finally



Effusion :

The effusion is the process of forcing a gas through a pin hole or small orifice from one compartment to another empty (vacuum) compartment.



Graham's Law :

Under similar condition of pressure (partial pressure) and temperature, the rate of diffusion of different gases is inversely proportional to square root of their density.

$\Rightarrow$ rate of diffusion, $\boxed{r \propto \frac{1}{\sqrt{d}}}$

$\Rightarrow \quad \frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \frac{\sqrt{V.D_2}}{\sqrt{V.D_1}}$

where, d = density of gas

V.D = vapour density

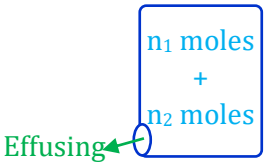
M = molar mass of gas

Under conditions of same temperature but different pressure, we have -

$\boxed{r \propto \frac{P}{\sqrt{M}}}$

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

If both gases are present in the same container at same temperature.



$$P \propto n$$

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

Rate of diffusion/effusion can be expressed as -

$$r = \frac{\text{volume diffused}}{\text{time taken}} \text{ or } \frac{\text{moles diffused}}{\text{time taken}} \text{ or } \frac{\text{pressure dropped}}{\text{time taken}}$$

$$\text{or } \frac{\text{distance travelled in horizontal tube of uniform cross-section}}{\text{time taken}}$$

Illustration 25:

32 ml of He effuses through a fine orifice in 1 minute. Then what volume of CH_4 will diffuse in 1 minute under the similar condition.

Solution:

$\because \quad r \propto \frac{1}{\sqrt{M}}$

$$r = \frac{\text{volume diffused}}{\text{time}}$$

$\because$ time is same so

$$\frac{V_{CH_4}}{V_{He}}=\sqrt{\frac{M_{He}}{M_{CH_4}}}$$

$$\frac{V_{CH_4}}{32}=\sqrt{\frac{4}{16}}$$

$$V_{CH_4}=\frac{1}{2}\times 32 = 16 \text{ mL.}$$

Illustration 26:

20 dm^3 of Ne diffuse through a porous partition in 60 seconds. What volume of SO_3 will diffuse under similar conditions in 30 sec. **(Atomic wt. of Ne = 20, S = 32)**

Solution:

$$\frac{r_{N_e}}{r_{SO_3}}=\sqrt{\frac{M_{SO_3}}{M_{Ne}}} \Rightarrow \qquad \frac{V_{Ne}/t_{Ne}}{V_{SO_3}/t_{SO_3}}=\sqrt{\frac{M_{SO_3}}{M_{Ne}}}$$

$$\Rightarrow V_{SO_3}=\frac{V_{Ne}\times t_{SO_3}}{t_{Ne}}\times\sqrt{\frac{M_{Ne}}{M_{SO_3}}}=\frac{20\times 30}{60}\times\sqrt{\frac{20}{80}}=\frac{10}{2}=5 \text{ dm}^3$$

Illustration 27:

A gaseous mixture of O_2 and X containing 20% (mole %) of X, diffused through a small hole in 234 seconds while pure O_2 takes 224 seconds to diffuse through the same hole. Molecular weight of X is :

Solution:

$$\frac{t_{mix}}{t_{O_2}} = \sqrt{\frac{M_{mix}}{M_{O_2}}}$$

$$\frac{234}{224} = \sqrt{\frac{M_{mix}}{32}}$$

$\therefore$ $M_{mix} = 34.921$.

As the mixture contains 20% (mole %) of X, the molar ratio of O_2 and X may be represented as 0.8n : 0.2n, n being the total no. of moles.

$$\therefore \quad M_{mix} = \frac{32\times 0.8n + M_x \times 0.2n}{n} = 34.921$$

$\therefore$ M_x (mol. wt. of X) = 46.6

Illustration 28:

At 1200°C, mixture of Cl_2 and Cl atoms (both in gaseous state) effuses 1.16 times as fast as krypton effuses under identical conditions. Calculate the fraction of chlorine molecules dissociated into atoms. M (Kr) = 83.8 g mol^{-1}.

Solution:

$Cl_2 \rightleftharpoons 2Cl$

$$\frac{r(Cl_2 \text{ and } Cl \text{ mix})}{r(Kr)} = 1.16 \sqrt{\frac{M(Kr)}{M_{av}(Cl_2 + Cl)}} = \sqrt{\frac{83.8}{M_{av}}}$$

$$\therefore \quad M_{av} = \frac{83.8}{(1.16)^2} = 62.28 \text{ g mol}^{-1}$$

	$Cl_2 \rightleftharpoons$	$2Cl$
Initial mole	1	0
After dissociation	(1 – x)	2x

(x = degree of dissociation)

Total moles after dissociation = 1 – x + 2x = (1 + x)

$$\therefore \quad \frac{(1-x)M(Cl_2) + 2x\,M(Cl)}{(1+x)} = 62.28 \Rightarrow \frac{(1-x)\times 71 + 2x \times 35.5}{1+x} = 62.28$$

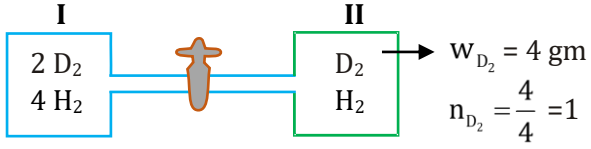
x = 0.14

$\therefore$ % dissociation = 14%

Illustration 29:

A mixture containing 2 moles of D_2 and 4 moles of H_2 is taken inside a container which is connected to another empty container through a nozzle. The nozzle is opened for certain time and then closed. The second bulb was found to contain 4 gm D_2. Then find % by moles of the lighter gases in second container.

Solution:



lighter gas = H_2

$$\frac{r_{H_2}}{r_{D_2}} = \frac{n_{H_2}}{n_{D_2}}\sqrt{\frac{M_{D_2}}{M_{H_2}}} = \frac{n'_{H_2}/t}{n'_{D_2}/t}$$

$$(\%\text{ mole of } H_2)_{II} = \left(\frac{n'_{H_2}}{n'_{H_2}+n'_{D_2}}\right)\times 100$$

$$\therefore \quad \frac{n_{H_2}}{n_{D_2}}\sqrt{\frac{M_{D_2}}{M_{H_2}}} = \frac{n'_{H_2}}{n'_{D_2}} \quad \Rightarrow \quad \frac{4}{2}\sqrt{\frac{4}{2}} = \frac{n'_{H_2}}{1}$$

$$\Rightarrow \quad n_{H_2} = 2\sqrt{2} \quad \Rightarrow \quad n_{D_2} = 1$$

$$(\%\text{ mole of } H_2)_{II} = \frac{(2\sqrt{2})}{(2\sqrt{2}+1)}\times 100 = \frac{2\times 1.44}{[(2\times 1.44)+1]}\times 100 = \frac{(2.8)}{(2.8+1)}\times 10 = 73.87\%$$

Illustration 30:

Why a heavier gas from a gas mixture effuses at slower rates ?

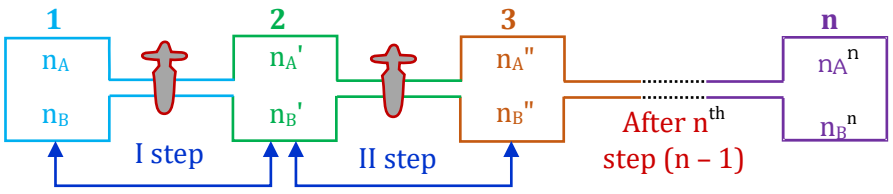
Solution:

In a gas mixture, the average kinetic energy of each gas $\left(\frac{1}{2}mv^2\right)$ is the same $\left(\frac{3}{2}RT\right)$. Hence, heavier gas has smaller speed.

Application of Graham's Law of Diffusion in Enrichment of Isotopes

Enrichment factor or Isotopic separation factor :

When two gases present in a container are allowed to diffuse in another container then gas having lower molecular mass will diffuse more and if this process is continued for large number of steps then we can obtain a mixture which is rich in a gas having lower molecular mass. Hence ultimately in the ultimate (last) container amount of lighter gas is larger as compared to heavier gas.



where, $M_A > M_B$ [similar condition of T and V] & $n_B^n >>>> n_A^n$

Enrichment factor (f) is defined as the ratio of final ratio of moles in the mixture [after n^{th} step] with initial mole ratio of the mixture.

$$f = \frac{\left(\frac{n_A^n}{n_B^n}\right)}{\left(\frac{n_A}{n_B}\right)} = \left(\sqrt{\frac{M_B}{M_A}}\right)^n = \frac{\text{final molar ratio}}{\text{initial molar ratio}}$$

Kinetic Theory of Gases

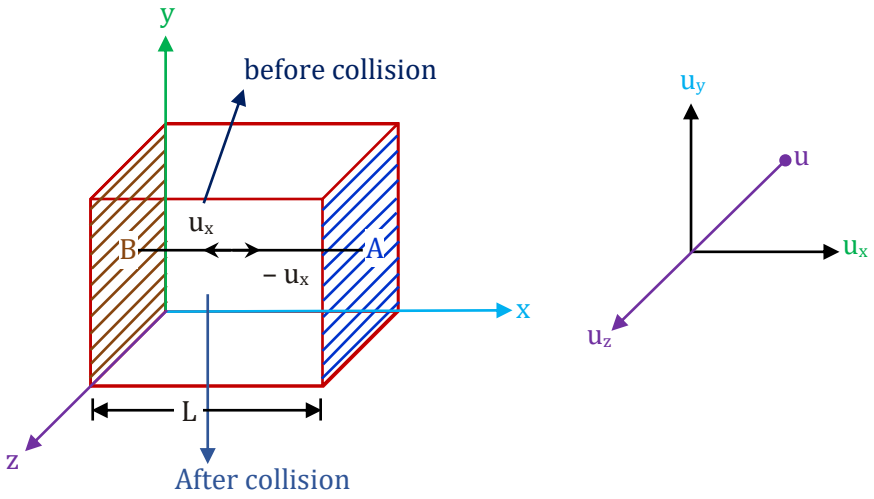
This is a theoretical model for ideal gas which can correlate the experimental facts (like Boyle's law, Charle's law& Avogadro's law etc.). It was presented by ***Bernoulli in 1738*** and developed in 1860 by ***Clausius, Maxwell, Kroning*** *and* ***Boltzmann***. Postulates of kinetic theory of gases are :

(i) All the gases consist of very small molecules or atoms whose volume is negligible compared to volume of container.

(ii) There are no attractive or repulsive forces between the molecules.
(iii) The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight line motion is known as Brownian motion)
(iv) Due to the continuous motion, collision between gaseous molecules and with the wall of container occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.
(v) The molecule moves with different speed; however the speed of each molecule keep on changing as the collision occur.
(vi) Collision among gas particles molecules is perfectly elastic, i.e., there is no loss in kinetic energy and moment during such collision.
(vii) The average kinetic energy of gas particles will depend on absolute temperature only.

Kinetic gas equation :

Let us consider a cube of side L, that has N molecules each of mass m moving with velocity u in all direction and thus colliding with one each other and against sides of the container. Velocity u can be resolved into three components u_x, u_y and u_z along there axis such that $u^2 = u_x^2 + u_y^2 + u_z^2$



For a simplest case we consider motion of a molecule along x-axis only in which it moves towards face B with velocity u_x. After collision against face B it moves towards face A with velocity $(-u_x)$ collision being elastic (which results in change in direction but not speed)

$\therefore$ Momentum before collision on face B = mu_x
Momentum after collision on face B = $-mu_x$
Change in momentum due to one collision on face B = $mu_x - (-mu_x) = 2mu_x$
To strike face B again distance travelled = 2L
Time taken to strike face B again = $\frac{2L}{u_x}$ seconds

$\therefore$ Number of collisions per second on face B along x-axis = $\frac{u_x}{2L}$

$\therefore$ Rate of change in momentum due to $\frac{u_x}{2L}$ collisions per second on face B along x-axis.

$= 2mu_x \cdot \frac{u_x}{2L} = \frac{mu_x^2}{L}$

Similarly, for y-axis change in momentum per second = $\frac{mu_y^2}{L}$ and for z-axis = $\frac{mu_z^2}{L}$

Net force by N molecules on a wall, $F_x = \frac{mu_{x_1}^2}{L} = \frac{mu_{x_2}^2}{L} + ... + \frac{mu_{x_N}^2}{L} = \frac{M}{L}.\Sigma u_x^2$

Now pressure = $\frac{\text{Force}}{\text{Area of six faces}} = \frac{\frac{m}{L}.\Sigma u_x^2}{L^2} = \frac{m.\Sigma u_x^2}{L^3} = \frac{m.\Sigma u^2}{V}$ [L^3 = volume V]

$\therefore$ $PV = m.\Sigma u_x^2$

As $\Sigma u_x^2 = \Sigma u_y^2 = \Sigma u_z^2$ and $\Sigma u_x^2 + \Sigma u_y^2 + \Sigma u_z^2 = \Sigma u^2$

$\therefore$ $PV = m.\Sigma u_x^2 = \frac{1}{3}\, m\, \Sigma u^2$.

$PV = \frac{1}{3} m \left(\frac{u_1^2 + u_2^2 + ...u_N^2}{N} \right).N$

$\therefore$ $PV = \frac{1}{3} mN u_{rms}^2$

This equation is called kinetic gas equation.

Kinetic energy of gas molecules :

Total translational K.E. of molecules

$= \frac{1}{2}mu_1^2 + \frac{1}{2}mu_2^2 + ... + \frac{1}{2}\, m.u_N^2 = \frac{1}{2} m.\Sigma u^2 = \frac{1}{2} mN.u_{rms}^2 = \frac{3}{2} PV = \frac{3}{2} nRT$

$\therefore$ Average translational K.E. per mole = $\frac{3}{2} RT$

and $(K.E.)_{\text{per molecule}} = \frac{3}{2}\left(\frac{R}{N_A}\right)T = \frac{3}{2} kT$

Where k = Boltzman constant = $\frac{R}{N_A} = \frac{8.314 J/mol K}{6.02 \times 10^{23}}$ = 1.3806×10^{-23} J K^{-1}

- $(K.E.)_{\text{per molecule}}$ and $(K.E.)_{\text{per mol}}$ is only depend on absolute temperature. It is does not depend on the nature of gas. This conclusion is known as ***"Maxwell's Generalisation"***.

Illustration 31:

Calculate the kinetic energy of 8 gram methane (CH_4) at 27°C temperature.

Solution:

$n = \frac{8}{16} = \frac{1}{2}$, T = (27° + 273) = 300 K, R = 8.314 J mol^{-1} K^{-1}

$(K.E.)_{n\,mol} = n \times \frac{3}{2} RT = \frac{1}{2} \times \frac{3}{2} \times 8.314 \times 300 = 1870.65$ J

Illustration 32:

Calculate the pressure exerted by 10^{23} gas molecules, each of mass 10^{-25} kg, in a container of volume 1×10^{-3} m^3 and having root mean square velocity of 10^3 ms^{-1}. Also calculate total kinetic energy and Temperature of the gas.

Solution:

By kinetic theory

$P = \frac{1}{3}\frac{mNu^2}{V} = \frac{1\times10^{-25}\times10^{23}\times(10^3)^2}{3\times10^{-3}} = 3.33 \times 10^6\ N\ m^{-2}$

Total KE $= \left(\frac{1}{2}mu_{rms}^2\right) \times N = \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4 = 0.5 \times 10^4\ J$

Also, total KE $= \frac{3}{2}nRT$, where, n (mole) $= \frac{10^{23}}{N_A} = \frac{10^{23}}{6.023\times10^{23}}$

$0.5 \times 10^4 = \frac{3}{2}\times\frac{10^{23}}{6.023\times10^{23}}\times8.314\times T$

$\therefore \quad T = \frac{0.5\times10^4\times2\times6.023}{3\times8.314} = 2415\ K$

Root Mean Square Velocity (u_{rms}) by kinetic gas equation :

$PV = \frac{1}{3}mNu_{rms}^2$

$\therefore \quad u_{rms} = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3RT}{M}}$

Different kind of speed of molecules :

(i) Average or mean speed, $u_{av} = \frac{u_1 + u_2 + ...+ u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$

(ii) Root mean square speed, $u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + ...+ u_N^2}{N}} = \sqrt{\frac{3RT}{M}}$

(iii) Most probable speed, $u_{mp} = \sqrt{\frac{2RT}{M}}$

It is the speed at which maximum fraction of molecules are travelling

Ratio of speeds :

$U_{rms} : U_{avg} : U_{mps} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}}$

$= \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.22 : 1.13 : 1 : 00 = 1.00 : 0.92 : 0.816$

Maxwell's Distribution of Speeds

It has already been pointed out that a gas is a collection of tiny particles separated from one another by large empty spaces and moving rapidly at random in all directions. In the course of their motion, they collide with one another and also with the walls of the container. Due to frequent collisions, the speeds and directions of motion of the molecules keep on changing. Thus, all the molecules in a sample of gas do not have same speed. Although it is not possible to find out the speeds of individual molecule, yet from probability considerations it has become possible to work out the distribution of molecules in different speed intervals. This distribution is referred to as the Maxwell-Boltzmann distribution in honour of the scientists who developed it. It may be noted that the distribution of speeds remains constant at a particular temperature although individual speeds of molecules may change.

$$dN = 4\pi N\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}}\, u^2 du = 4\pi N\left[\frac{m}{2\pi kT}\right]^{3/2} e^{\frac{-mu^2}{2KT}}.u^2.du$$

Here, dN = Number of molecules having speeds between u and u + du.

N = Total number of molecules.

M = Molar mass of gas (kg/mol)

u = Root mean square velocity

du = Velocity interval

$$\frac{dN}{N} = 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}}\, u^2 du$$

Here, dN / N = fraction of molecules having speeds between u and u + du.

and $\frac{1}{N}\left(\frac{dN}{du}\right)$ = fraction of molecules having speed between u to u + du per unit interval of speed.

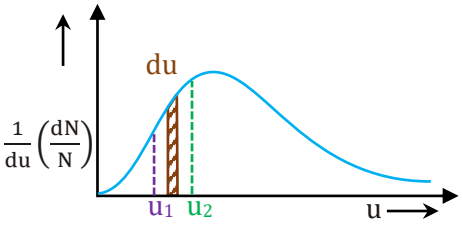
= Maxwell distribution function.

According to this expression, the fraction $\frac{dN}{N}$ of molecules depends only on temperature having speeds between u and u + du for a gas of molar mass M. Thus, for a given temperature, this fraction has a constant value.

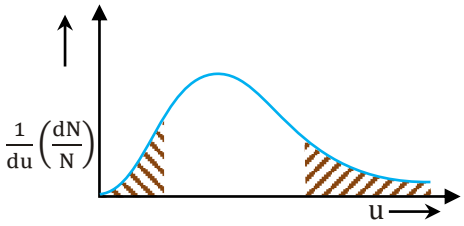
Properties of Maxwell's graph :

I. Area between u_1 and u_2 = $\int_{u_1}^{u_2} \frac{1}{du}\left(\frac{dN}{N}\right)du = \int_{u_1}^{u_2}\left(\frac{dN}{N}\right)$

Hence, total fraction of particles with speed between u_1 and u_2 = Area under the curve represents fraction of molecules.

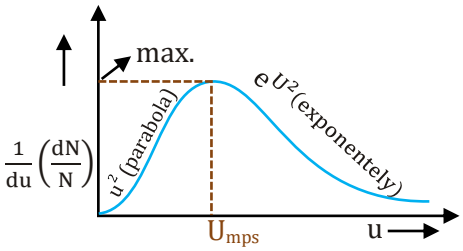


II.

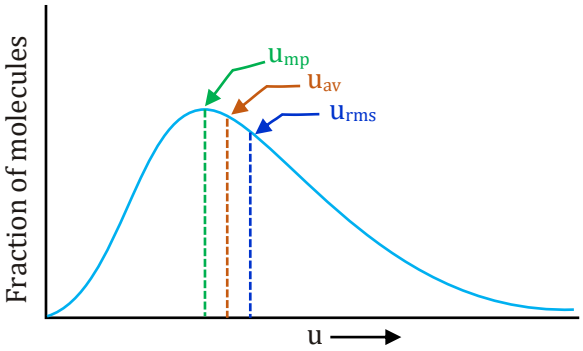


It can be seen from the above figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers.

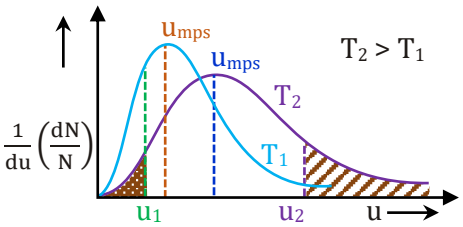
III. The curve at any temperature is parabolic near the origin, since the factor u^2 is dominant in this region, the exponential function being approximately equal to unity. At high values of u, however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed (u_{mps}). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.



IV. Graph between fraction of molecules vs molecular speeds :

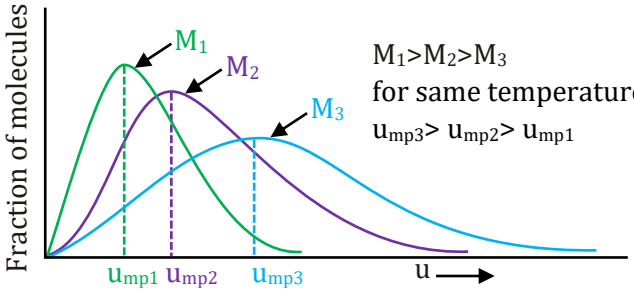


V. Total area under the curve will be constant and will be unity at all temperatures. The above figure illustrates the distribution of speeds at two temperatures T_1 and T_2. Since the total no. of molecules is same at both temperatures, increase in the K.E. of the molecules results decrease in fraction of molecules having lower speed range and increase in fraction of molecules having higher speed range on increasing the temperature.



On increasing temperature, the value of u_{mps} (most probable speed) will increase. Also, the curve at the higher temperature T_2 has its u_{mps} shifted to a higher value compared with that for T_1, whereas corresponding fraction of molecules has decreased. But at the same time, the curve near u_{mps} has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

VI.



At a given temperature u_{mps} will be more for lighter gas (M_3) but fraction of molecules moving with u_{mps} will be more for heavier gas (M_1).

Note :

Effect of M and T are opposite.

Maxwell Distribution of kinetic energy :

By Maxwell equation : $dN = 4\pi N\left(\frac{M}{2\pi RT}\right)^{3/2} . e^{\frac{-Mu^2}{2RT}} u^2.du$

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

The shaded area of this graph indicates the fraction of particles having energy between E_1 and E_2

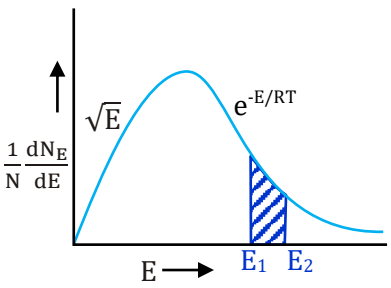


Illustration 33:

Four particles have speed 2, 3, 4 and 5 cm/s respectively. Find their avg. & rms speed :

Solution:

$$U_{avg.} = \frac{U_1 + U_2 + U_3 + ...U_N}{N}$$

$$U_{avg.} = \frac{2+3+4+5}{4} = 3.5\,cm/s$$

$$U_{r.m.s.} = \sqrt{\frac{U_1^2 + U_2^2 + U_3^2 + ...}{N}}$$

$$u_{rms} = \sqrt{\frac{2^2+3^2+4^2+5^2}{4}} = \frac{\sqrt{54}}{2}\,cm/s$$

Illustration 34:

At what temperature do the average speed of $CH_{4(g)}$ molecule equal the average speed of O_2 molecule at 300 K ?

Solution:

$$(U_{avg})_{CH_4} = (U_{avg})_{O_2}$$

$$\sqrt{\frac{8RT}{\pi \times 16}} = \sqrt{\frac{8 \times R \times 300}{\pi \times 32}}$$

T = 150 K

Illustration 35:

At 27°C find the ratio of root mean square speeds of ozone to oxygen :-

Solution:

$$\frac{U_{rms}(O_3)}{U_{rms}(O_2)} = \sqrt{\frac{\frac{3RT}{M.W_{O_3}}}{\frac{3RT}{M.W_{O_2}}}} = \sqrt{\frac{M.W_{O_2}}{M.W_{O_3}}} = \sqrt{\frac{32}{48}} = \sqrt{\frac{2}{3}}$$

Illustration 36:

The temperature at which U_{rms} of He becomes equal to U_{mp} of CH_4 at 500 K.

Solution:

$$(U_{rms})_{He} = (U_{mp})_{CH_4}$$

$$\sqrt{\frac{3RT_{He}}{M_{He}}} = \sqrt{\frac{2RT_{CH_4}}{M_{CH_4}}}$$

$$\frac{3T}{4} = \frac{2 \times 500}{16}$$

$$T = \frac{250}{3}K$$

Illustration 37:

Calculate the root mean square speed of H_2 molecules under following condition.

(a) 2 mole of H_2 at 27°C.

(b) 3 mole of H_2 in a 5 lit container at 10^5 Pa.

(c) 4 mole of H_2 at the density of 1 gm/ml at 10^5 Pa.

Solution:

(a) $U_{r.m.s.} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times 8.314 J/molK\times 300K}{2\times 10^{-3} kg}} = 1934.24$ m/sec.

(b) $U_{r.m.s.} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3\times 10^5 Pa\times 5\times 10^{-3} m^3}{3mol\times 2\times 10^{-3} kg}} = 500$ m/sec.

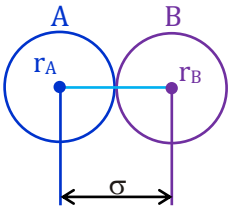
(c) $U_{r.m.s.} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3\times 10^5 Pa}{10^3 kg/m^3}} = 17.32$ m/sec.

Collision parameters :

Assumption :

All the particles (molecules or atoms) have rigid, similar shape and size and are spherical in nature that will not change after collision.

Collision diameter : It is the closest distance between the centres of two molecules taking part in collision.



Collision diameter (σ) = $r_A + r_B$

Collision Frequency :

It is the total number of molecular collisions taking place per second per unit volume of the gas.

The no. of collisions made by a single molecule with other molecules per unit time **(collision number)** are given by $Z_1 = \sqrt{2}\,\pi\sigma^2 U_{avg} N^*$

The total number of bimolecular collision per unit time per unit volume is given as Z_{11} **(collision frequency)**

$$Z_{11} = \frac{1}{2}(Z_1 N^*) = \frac{1}{2} \times N^* \times \sqrt{2}\,\pi\sigma^2 U_{avg} N^*$$

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 U_{avg} N^{*2}$$

If the collisions involve two unlike molecules, the no. of bimolecular collision is given as Z_{12}.

$$Z_{12} = \pi\sigma_{12}^2 \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} N_1^* N_2^*$$

Where N_1^* and N_2^* are the no. of molecules per unit volume of the two types of gases, σ_{12} is the average diameter of two molecules, that is $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$ & μ is the reduced mass, that is $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$, m_1 & m_2 are the mass of single molecule respectively 1 and 2.

Mean free path :

The mean free path is the average distance travelled by a molecule between two successive collisions. We can express it as follows :

$$\lambda = \frac{\text{distance travelled per unit time}}{\text{No. of collsions made by single molecule per unit time}}$$

$$= \frac{U_{avg}}{Z_1} = \frac{U_{avg}}{\sqrt{2}\pi\sigma^2 U_{avg} N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

Wall collision : It represents the total number of molecules colliding at the wall per unit area per unit time.

$$Z_w = \frac{1}{4}.N^*.u_{av} = \frac{P.N_A}{\sqrt{2\pi MRT}}$$

Rate of effusion :

If the corss-section area of orifice in the vessel is 'A', then the number of molecules effusing out per unit time is

$$r_{eff.} = Z_w.A = \frac{P.N_A.A}{\sqrt{2\pi MRT}}$$

Illustration 38:

Calculate λ, Z_1 and Z_{11} for oxygen at 298 K and 10^{-3} mm Hg. Given $\sigma = 3.61 \times 10^{-8}$ cm.

Solution:

$$N^* = \frac{P}{kT} = \frac{10^{-3} \times 101325}{760 \times 1.38 \times 10^{-23} \times 298} = 0.324 \times 10^{20}$$

$$U_{avg} = \sqrt{\frac{8}{\pi}\frac{RT}{M}} = \sqrt{\frac{8}{3.14} \times \frac{8.314 \times 298}{32 \times 10^{-3}}} = 444.138 \text{ m/sec}$$

$$Z_1 = \sqrt{2}\,\pi\,\sigma^2\,U_{avg}\,N^* = \sqrt{2} \times 3.14 \times 3.61 \times 10^{-10}\text{ m} \times 444.138\text{ m} \times 0.324 \times 10^{20} = 8.326 \times 10^3\text{ sec}^{-1}$$

$$Z_{11} = \frac{1}{2} Z_1 N^* = \frac{1}{2} \times 8.326 \times 10^3\text{ sec}^{-1} \times 0.324 \times 10^{20} = 13.488 \times 10^{22}\text{ m}^{-3}\text{ sec}^{-1};$$

$$\lambda = \frac{U_{avg.}}{Z_1} = \frac{444.138\text{ m/sec}}{8.326 \times 10^3\text{ sec}^{-1}} = 5.334 \times 10^{-2}\text{ m}$$

Illustration 39:

Two flask A and B have equal volume. A is maintained at 300 K and B at 600 K while A contains H_2 gas, B has an equal mass of CH_4 gas. Assuming ideal behaviour for both the gases, find the following.

(a) Flask containing greater number of moles

(b) Flask in which pressure is greater

(c) Flask in which U_{avg} of the molecules are greater

(d) Flask with greater mean free path of molecules (Collision diameters of H_2 & CH_4 may be taken same)

(e) Flask with greater molar kinetic energy.

(f) Flask in which the total kinetic energy is greater

(g) Flask in which Z_1 and Z_{11} are greater

Solution:

(a) $N_{H_2} = \frac{m}{2}N_A ; N_{CH_4} = \frac{m}{16}N_A$

$\therefore$ molecules of H_2 in flask A > molecules of CH_4 in flask B

(b) $P_AV = n_ART_A ; P_BV = n_BRT_B$

$\Rightarrow \frac{P_A}{P_B} = \frac{n_AT_A}{n_BT_B} = \frac{m/2}{m/16} \times \frac{300}{600} = 4$

$\therefore$ pressure of H_2 in flask A > pressure of CH_4 in flask B

(c) $(U_{avg})_A = \sqrt{\frac{8}{\pi}\frac{RT_A}{M_A}}$; $(U_{avg})_B = \sqrt{\frac{8}{\pi}\frac{RT_B}{M_B}}$

$\frac{(U_{avg})_A}{(U_{avg})_B} = \sqrt{\frac{T_A}{T_B}\frac{M_B}{M_A}} = \sqrt{\frac{300}{600} \times \frac{16}{2}} = 2$

$\therefore$ U_{avg} of H_2 in flask A > U_{avg} of CH_4 in flask B

(d) $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 \times P} \times kT$ [where N* = P/kT]

$\frac{\lambda_A}{\lambda_B} = \frac{T_A}{T_B} \times \frac{P_B}{P_A} = \frac{300}{600} \times \frac{1}{4} = \frac{1}{8}$

$\therefore$ $\lambda_B > \lambda_A$

(e) molar K.E. = $\frac{3}{2}RT$

$\therefore$ $T_B > T_A$

$\therefore$ KE of CH_4 in flask B > KE of H_2 in flask A

(f) $(KE)_{total} = \frac{3}{2}RT \times n$

$\frac{(KE)_{T,A}}{(KE)_{T,B}} = \frac{(300 \times \frac{m}{2})}{(600 \times \frac{m}{16})} = \frac{1}{2} \times 8 = 4$

$\therefore$ $(KE)_{T,A} > (KE)_{T,B}$

(g) (i) $Z_1 = \sqrt{2}\pi\sigma^2 U_{avg} N^*$

$\frac{(Z_1)_A}{(Z_1)_B} = \frac{(U_{avg})_A}{(U_{avg})_B} \times \frac{N_A^*}{N_B^*} = 2 \times \frac{N_A}{N_B} = 2 \times 8 = 16$

$\therefore$ $(Z_1)_A > (Z_1)_B$ $(Z_1)_A > (Z_1)_B$

(ii) $Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 U_{avg} N^{*2}$

$\frac{(Z_{11})_A}{(Z_{11})_B} = \frac{(U_{avg})_A}{(U_{avg})_B} \times \frac{(N_A^*)^2}{(N_B^*)^2} = 2 \times \frac{N_A}{N_B} = 2 \times 8^2 = 128$

$\therefore$ $(Z_{11})_A > (Z_{11})_B$

Eudiometry :

Eudiometry or gas analysis involves the calculations based on gaseous reactions or the reactions in which at least two components are gaseous, in which the amounts of gases are represented by their volumes, measured at the same pressure and temperature. Some basic assumptions related with calculations are:

(i) Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.

$N_2(g)$ + $3H_2(g)$ $\longrightarrow$ $2NH_3(g)$

1 vol. 3 vol. 2 vol.

Problem may be solved directly is terms of volume, in place of mole. The stoichiometric coefficients of a balanced chemical reactions gives the ratio of volumes in which gaseous substances are reacting and products are formed, at same temperature and pressure.

(ii) The volumes of solids or liquids is considered to be negligible in comparison to the volume of gas. It is due to the fact that the volume occupied by any substance in gaseous state is even more than thousand times the volume occupied by the same substance in solid or liquid states.

$2H_2(g)$ + $O_2(g)$ $\longrightarrow$ $2H_2O(l)$

2 mole 1 mole 2 mole

2 vol. 1 vol. 0 vol.

(iii) Air is considered as a mixture of oxygen and nitrogen gases only. It is due to the fact that about 99% volume of air is composed of oxygen and nitrogen gases only.

(iv) Nitrogen gas is considered as a non-reactive gas. It is due to the fact that nitrogen gas reacts only at very high temperature due to its very high thermal stability. Eudiometry is performed in a eudiometer tube and the tube cannot withstand very high temperature. This is why, nitrogen gas cannot participate in the reactions occurring in the eudiometer tube.

(v) The total volume of non-reacting gaseous mixture is equal to sum of partial volumes of the component gases **(Amagat's law)**.

$V = V_1 + V_2 +$.....

Partial volume of gas in a non-reacting gaseous mixture is its volume when the entire pressure of the mixture is supposed to be exerted only by that gas.

(vi) The volume of gases produced is often given by certain solvent which absorb contain gases.

Solvent	**Gases absorb**
KOH	CO_2, SO_2, Cl_2
Ammonical Cu_2Cl_2	CO
Turpentine oil	O_3
Alkaline pyrogallol	O_2
water	NH_3, HCl
$CuSO_4/CaCl_2$	H_2O

(vii) EUDIOMETER

A eudiometer is a laboratory device that measures the change in volume of a gas mixture following a physical or chemical change.

Illustration 40:

10 ml of CO is mixed with 25 ml air (20% O_2 by volume). Find final volume (in ml) after complete combustion.

Solution:

$$\overset{10ml}{CO} + \overset{5ml}{\frac{1}{2}O_2} \longrightarrow \underset{10ml}{CO_2}$$

$V_f = V_{CO_2}$ + Volume of remaining air = 10 + 20 = 30 ml

Illustration 41:

A 3 L gas mixture of propane (C_3H_8) and butane (C_4H_{10}) on complete combustion at 25°C produced 10 L CO_2. Assuming constant P and T conditions what was volume of butane present in initial mixture ?

Solution:

$C_3H_8(g) + 5O_2 \longrightarrow 3CO_2(g) + 4H_2O(l)$

x L 3x L

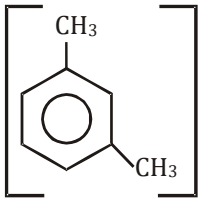
$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$

(3-x) L 4(3 – x) L

from question $3x + 4(3 - x) = 10 \Rightarrow x = 2$

$\therefore$ Volume of butane, $C_4H_{10} = (3 - x) = 1$ L

Illustration 42:

100 ml gaseous meta Xylene  undergoes combustion with excess of oxygen at room temperature and pressure. Volume contraction / expansion (in ml) during reaction is

Solution:

$C_8H_{10}(g) + \frac{21}{2}O_2(g) \longrightarrow 8CO_2(g) + 5H_2O(l)$

100 ml $\frac{21}{2}\times 100 = 1050ml$ 800 ml 0

$\therefore$ Contraction in volume = (100 + 1050) – 800 = 350 ml

Illustration 43:

An alkene upon combustion produces $CO_2(g)$ and $H_2O(g)$. In this combustion process if there is no volume change occurs then the no. of C atoms per molecule of alkene will be :

Solution:

$C_nH_{2n}(g) + \frac{3n}{2}O_2(g) \rightarrow nCO_2(g) + nH_2O(g)$

if there no volume changes i.e. $\Delta_{ng} = 0$

$(n + n) - \left(1 + \frac{3n}{2}\right) = 0 \Rightarrow n = 2$

Illustration 44:

A gaseous hydrocarbon (C_xH_y) requires 6 times of its own volume of O_2 for complete oxidation and produces 4 times of its volume of CO_2. Find out the volume of x + y.

Solution:

$C_xH_y + (x + \frac{y}{4})\, O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O(l)$

a $\quad a\left(x+\frac{y}{4}\right)$ $\quad ax$

Given that : $a(x + y/4) = 6a$

and $\quad ax = 4\ (a)$

$x = 4$ and $y = 8$

$\therefore \quad x + y = 4 + 8 = 12$

Illustration 45:

On heating 60 ml mixture containing equal volume of chlorine gas and it's gaseous oxide, volume becomes 75 ml due complete decomposition of oxide. On treatment with KOH volume becomes 15 ml. What is the formula of oxide of chlorine ?

Solution:

Let oxide of Cl is Cl_xO_y

So, in 60 mL $\Rightarrow$ 30 mL Cl_xO_y and 30 mL Cl_2.

Now,

$Cl_xO_y \longrightarrow \frac{x}{2}Cl_2 + \frac{y}{2}O_2$

30mL

$\frac{30.x}{2}$mL $\quad \frac{30.y}{2}$mL

Given :

$75 = 30 + \frac{30x}{2} + \frac{30y}{2} \Rightarrow x + y = 3 \qquad ...(i)$

KOH absorbs Cl_2 and volume becomes 15 mL so,

$(75 - 15) = V_{Cl_2} = 30 + \frac{30x}{2} \Rightarrow x = 2$ and $y = 1$

So the oxide : Cl_2O

Illustration 46:

5 L of A (g) & 3 L of B(g) measured at same T & P are mixed together which react as follows

$$2A(g) + B(g) \rightarrow C\ (g)$$

What will be the total volume (in litre) after the completion of the reaction at same T & P.

Solution:

$2A(g) + B(g) \longrightarrow C(g)$

5L $\quad$ 3L

L.R. is A

So, volume of C produced = $\frac{1}{2} \times 5 = 2.5$ L

and, volume of B reacted = $\frac{1}{2} \times 5 = 2.5$ L

So, volume of B remained = 3 – 2.5 = 0.5 L

Hence, $V_{total} = V_C + V_B = 2.5 + 0.5 = 3$ L

Real Gas

Introduction:

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually, no gas is ideal or perfect in nature. All gases are real gases.

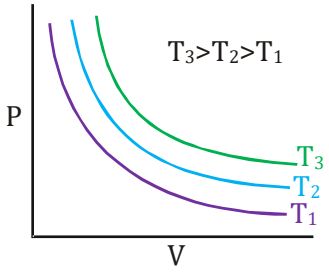
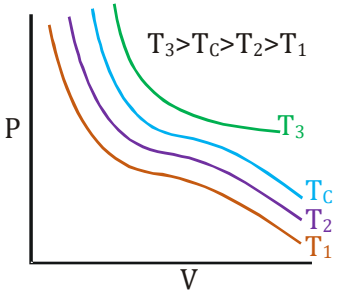
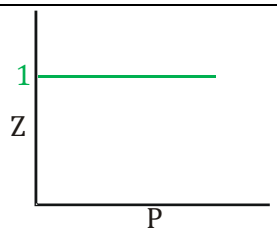
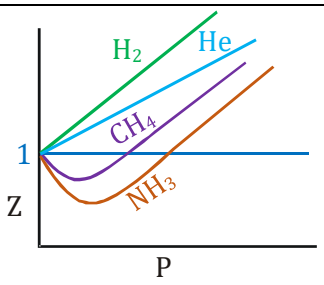
Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.

Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

(i) The volume of gas particle is negligible compared to volume of container (while the real gas particle may have some significant volume).

(ii) There is no interaction between gaseous particles (while attraction forces exist between real gas particles).

Comparison between Real and Ideal gas :

IDEAL GAS		REAL GAS	
(i)	PV = nRT	**(i)**	$PV \neq nRT$ $\Rightarrow$ If PV > nRT (Gas is less compressible than ideal gas). If PV < nRT (Gas is more compressible than ideal gas).
(ii)	No liquefaction is possible. 	**(ii)**	Liquefaction is possible below a certain temperature.  $\Rightarrow$ Follow critical phenomena and cannot liquefy above T_C.
(iii)		**(iii)**	
(iv)	No interaction force is present between gas particles.	**(iv)**	Interaction force exist between gas particles which vary depending upon conditions.
(v)	Volume of gas particles is negligible cannot w.r.t. volume of container.	**(v)**	Volume of gas particles has significant value and be neglected normally w.r.t. volume of container.

Vander Waal Equation of real gases

The ideal gas equation does not consider the effect of attractive forces and molecular volume.

Vander Waal corrected the ideal gas equation by taking the effect of

(a) Molecular volume

(b) Molecular attraction

(A) Volume correction :

In the ideal gas equation, $P_iV_i = nRT$, V_i represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume V_i is the total volume V minus the volume occupied by the gas molecules.

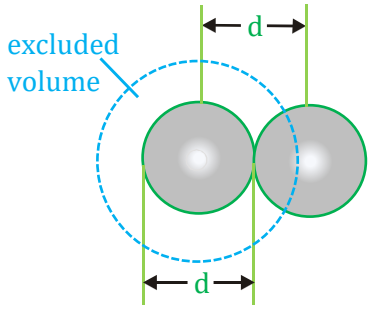


Illustration of excluded volume

Real volume of gas = Actual volume of container – volume occupied by molecules in motion.

$V_i = V - nb$ for n mole of gas

Where b is termed the 'excluded volume' or 'co-volume' per mole.

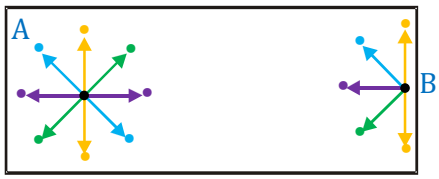
It is constant and characteristic for each gas.

$b = 4 \times$ volumes of one molecule $\times N_A = 4 \times \frac{4}{3}\pi r^3 N_A = \frac{16}{3}\pi r^3 N_A$

(B) Pressure correction :

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A in the midst of the vessel.

This molecule is surrounded by other molecules in a symmetrical manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction.



Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only in one side of the vessel, i.e. towards its centre, with the result of that, this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas.

Vander Waals noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules, n/V. However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration n/V. Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas wall by a factor proportional to n^2/V^2. Letting a be the proportionality constant, we can write

$$P\text{ (actual)} = P\text{(ideal)} - \frac{an^2}{V^2} \text{ or} \qquad P\text{ (ideal)} = P\text{(actual)} + \frac{an^2}{V^2}$$

'a' is a constant which depends upon the nature of the gas,

Combining the two corrections, for 1 mole of gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{and for n mole of gas} \quad \left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The constants 'a' and 'b' :

Vander Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

(i) The 'a' value for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.

(ii) The gas having higher value of 'a' can be liquefied easily and therefore H_2 and He are not liquefied easily.

(iii) Unit of 'a' is atm lit^2 $mole^{-2}$ or dyne cm^4 $mole^{-2}$ or Nm^4mol^{-2}

(iv) Unit of 'b' is lit $mole^{-1}$ or cm^3 $mole^{-1}$ or m^3 mol^{-1}

The van der Walls constants for some common gases

Gas	a ($atmL^2mol^{-2}$)	b ($L\ mol^{-1}$)
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562
Ethane	5.49	0.0638
Ethanol	2.56	0.087
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0433
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	3.71	0.0564
Water	5.44	0.0305

Compressibility factor (Z) :

The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z),

$$Z = \frac{(PV)_{real}}{(PV)_{ideal}} = \frac{V_m}{V_{m(ideal)}} = \frac{PV_m}{RT} \qquad [V_m = \text{molar volume}]$$

Plots of compressibility factor vs pressure :

(i) For an ideal gas Z = 1 and is independent of temperature and pressure.

(ii) Exceptional behaviour of H_2 and He :

For these gases Z > 1 at 0ºC.

(iii) Effect of pressure :

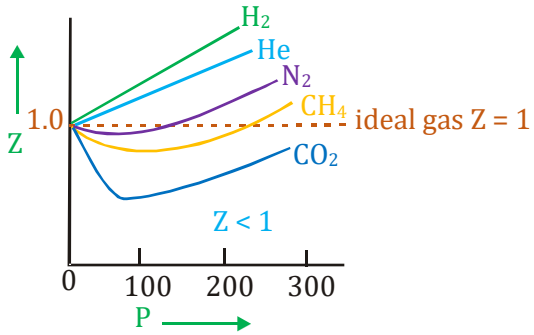
At very low P, $PV_m \approx RT$ i.e. $Z \approx 1$

At low P, $PV_m < RT$ i.e. $Z < 1 \Rightarrow$ attractive forces dominant

At high P, $PV_m > RT$ i.e. $Z > 1 \Rightarrow$ repulsive forces dominant

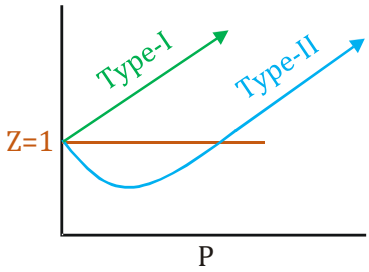
(iv) For the gases which are easily liquefied (e.g. CO_2) Z dips sharply below the ideal line in the low-pressure region.

(v) Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours, Z approaches unity with increase in temperature.



Verification of compressibility factor using Vander Waal's equation :

Variation of Z with P for real gas at any temperature is given by following graph.



Vander Waal equation :

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

(i) At low pressure and constant temperature

At low pressure V_m will be high hence b can be neglected in comparison to V_m. But $\frac{a}{V_m^2}$ can't be neglected as pressure is low. Thus, equation would be

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

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

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

$$\mathbf{Z = 1 - \frac{a}{V_m RT}} \Rightarrow \quad Z < 1$$

Substituting $V_m = \frac{RT}{P}$ in above equation ; $\mathbf{Z = 1 - \frac{aP}{R^2T^2}}$

At low pressure, real gas is easily compressible as compared to an ideal gas.

(ii) At high pressure and constant temperature

At high pressure the V_m will be low. So, b can't be neglected in comparison to V_m but $\frac{a}{V_m^2}$ can be neglected as compared to much higher values of P.

Then van der Waals' equation will be

$P(V_m - b) = RT$

$PV_m - Pb = RT$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$\mathbf{Z = \frac{Pb}{RT} + 1} \Rightarrow (Z > 1)$$

At high pressure, gas is more difficult to compress as compared to an ideal gas.

(iii) At low pressure and very high temperature.

V_m will be very large, hence 'b' can be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large.

$PV_m = RT$ (ideal gas condition)

(iv) For H_2 or He $a \simeq 0$ because molecules are smaller in size or Vander Waal's forces will be very weak.

$P(V_m - b) = RT$

So, $\mathbf{Z = 1 + \frac{Pb}{RT}}$

This explains type I plot.

Illustration 1:

Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using Vander Waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that a = 3.592 atm lt^2 mol^{-2}, b = 0.0427 L/mol. Also, if the volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K.

Solution:

Vander Waal's equation

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

$n_{CO_2} = 5$, V = 1 litre, T = 320 K, a = 3.592, b = 0.0427

$$\therefore \quad \left[P + 25 \times \frac{3.592}{1}\right] [1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

$\therefore$ P = 77.218 atm

For ideal behaviour of gas, PV = nRT

$\therefore$ P × 1 = 5 × 0.0821 × 320

$\therefore$ P = 131.36 atm

For one mole $\left[P + \frac{a}{V^2}\right] [V - b] = RT$

$$\therefore \quad P = \frac{RT}{V} - \frac{a}{V^2}$$

$\therefore \quad P = \frac{0.0821\times273}{22.4} - \frac{3.592}{(22.4)^2}$

$\therefore \quad P = 0.9922$ atm

The volume occupied by 1 mole at 273 K is 22.4 litre if b is negligible.

Illustration 2:

One mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If Vander Waal's constants are a = 20.39 L^2 atm mol^{-2} and b = 0.1383 L mol^{-1}, calculate compressibility factor Z under,

(a) low pressure region. (b) high pressure region.

Solution:

(a) Under low pressure region, V is high

$\therefore \quad (V - b) \approx V$

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

$$PV + \frac{a}{V} = RT \quad \Rightarrow \quad \frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left(1 - \frac{a}{RTV}\right) = 1 - \frac{20.39}{0.0821\times350\times35} = 0.98$$

(b) Under high pressure region, P is high,

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

$\therefore \quad P(V - b) = RT$

$PV - Pb = RT$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore \quad Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}\,\frac{Pb}{RT} \qquad \left(\because \frac{PV}{RT} = 1, \text{ or } \frac{P}{RT} = \frac{1}{V}\right)$$

$$Z = 1 + \frac{b}{V} = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

Illustration 3:

One way of writing the equation of state for real gases is $PV = RT\left[1 + \frac{B}{V} + ...\right]$ where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.

Solution:

According to van der Waal's equation

$$\left[P + \frac{a}{V^2}\right][V - b] = RT \qquad \text{or} \qquad P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

Multiply by V, then

$$PV = \frac{RT}{(V-b)} - \frac{a}{V} \qquad \text{or} \qquad PV = RT\left[\frac{V}{V-b} - \frac{a}{VRT}\right] \text{ or } \qquad PV = RT\left[\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{VRT}\right]$$

$$\because \quad \left[1 - \frac{b}{V}\right]^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + ...$$

$\therefore \quad PV = RT\left[1+\frac{b}{V}+...-\frac{a}{VRT}\right]$

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

$\therefore \quad B = b - \frac{a}{RT}$

Boyle temperature :

(i) It is temperature at which a real gas behaves ideally in a wide range of pressure.

(ii) (a) Temperature < Boyle temperature

$Z < 1$, low pressure range

$Z > 1$, high pressure range

(b) Temperature = Boyle temperature

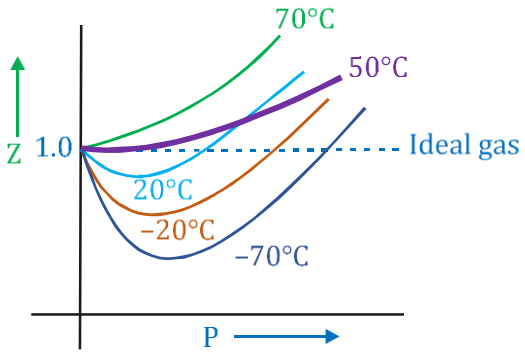
$Z = 1$, low pressure range

$Z > 1$, high pressure range

(c) At temperature > Boyle temperature

$Z > 1$, at all pressure

(d) $T \to \infty, Z \to 1$



On increasing the temperature, the thermal energy increases and simultaneously the attractive forces decrease. Hence a temperature comes at which the thermal energy become too high that it balances the effect of attraction and gas molecules becomes independent.

If at Boyle temperature, pressure is increased, molecules come closer. Due to repulsive force, Z becomes greater than 1.

Calculation of TB :

(i) $PV_m = RT = \left(1+\frac{B}{V_m}+\underbrace{\frac{C}{V_m^2}+.....}_{\text{negligible}}\right)$ at low pressure.

At $T = T_B$, the second initial coefficient should be 0

$B = 0$

or $b-\frac{a}{RT_B}=0$

$\therefore \quad \boxed{T_B=\frac{a}{Rb}}$

(ii) Calculus method :

At Boyle temperature, $\left(\frac{\partial Z}{\partial P}\right)_T = 0$ at low pressure.

Illustration 4:

Derive the expression for compressibility factor of a Vander Waal gas at Boyle temperature.

Solution:

$Z=\frac{V_m}{V_m-b}-\frac{a}{V_m-RT}$

At Boyle temperature,

$$Z=\frac{V_m}{V_m-b}-\frac{a}{V_mR\times\frac{a}{Rb}}=\frac{V_m}{V_m-b}-\frac{b}{V_m}$$

$$Z=\frac{V_m^2-V_mb+b^2}{V_m(V_m-b)}$$

$$Z=1+\frac{b^2}{V_m(V_m-b)}$$

Illustration 5:

Calculate the volume occupied by 2 moles of a Vander Waal gas at 5 atm 800 K.

Given : a = 4.0 atm l^2mol^{-2} l, b = 0.0625 mol^{-1} l, R = 0.08 -atm/K-mol

Solution:

$$T_B=\frac{a}{Rb}=800K$$

Gas behave ideally at given condition.

PV = nRT

5 × V = 2 × 0.08 × 800

V = 25.6 litre

Liquefaction of gases and Critical points :

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they exist in liquid state. A gas can be liquefied by :

(a) Increasing pressure : An increase in pressure results decrease in intermolecular distance.

(b) Decreasing temperature : A decrease in temperature results decrease in kinetic energy of molecules.

Note : Due to absence of intermolecular forces, ideal gases can never be liquified.

Andrews Isotherms :

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for CO_2.The types of isotherms are shown in figure.

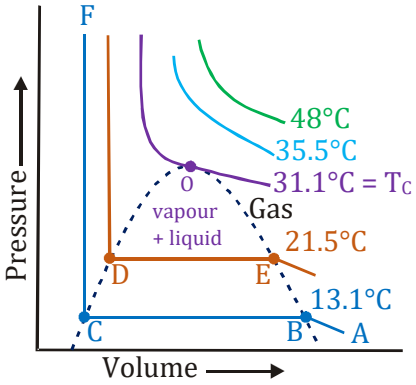


Fig : Isotherms for carbon dioxide

Observations from figure :

(a) At low temperatures : For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B). At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density). At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium and CF represent liquid state.

The pressure corresponding to the line BC is vapour pressure of the liquid at that temperature.

(b) At lower temperatures : Similar type of curve as in case (A) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.

(c) At high temperatures : (say 48°C), the isotherms are like those of ideal gas. Gas does not liquify, even at very high pressure.

(d) At temperature (31.1°C) : The horizontal portion is reduced to a point.

The isotherm at T_C is called **critical isotherm**.

At point O, $\frac{dP}{dV} = 0$.

The point O is called the **point of inflection**.

Critical parameters or critical constants :

Critical temperature (T_C) : The temperature above which a system can never be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exit is called the critical temperature T_C.

Critical pressure (P_C) : The minimum pressure required to liquefy the system at the temperature T_C is called the critical pressure P_C.

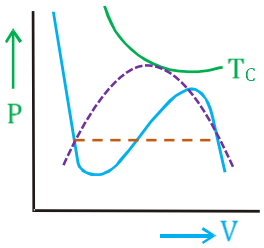
Critical volume (V_C) : The volume occupied by one mole of the system at critical temperature, T_C and critical pressure, P_C is called the critical volume (V_C) of the gas.

Determination of value of P_C, V_C and T_C :

The Vander Waal's equation is

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

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



This equation has three roots in V_m for given values of a, b, P and T. It is found that either all the three roots are real or one is real and the other two are imaginary.

At temperature lower than T_C, the isotherm exhibits a maximum and a minimum for certain values of pressures, the equation gives three roots of volume e.g., V_1, V_2 and V_3 at pressure P_1. On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation V_m can be written as

$$(V_m - V')(V_m - V'')(V_m - V''') = 0$$

At the critical point $V' = V'' = V''' = V_C$

$\therefore$ the equation becomes,

$$(V_m - V_C)^3 = 0$$

or $$V_m^3 - V_C^3 - 3V_C V_m^2 + 3V_C^2 V_m = 0 \quad ...(2)$$

By comparing the coefficients in eq.(1) and eq(2)

$$3V_C = b + \frac{RT_C}{P_C},\ 3V_C^2 = \frac{a}{P_C},\ V_C^3 = \frac{ab}{P_C}$$

By solving, $\mathbf{V_C = 3b,\ P_C = \frac{a}{27b^2}}$ **and** $\mathbf{T_C = \frac{8a}{27Rb}}$

The value of critical compressibility factor in terms of Vander wall's constants is given by

$$Z = \frac{P_C V_C}{RT_C} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}} = \frac{3}{8} = 0.375$$

If we compare the value of $\frac{P_C V_C}{RT_C} = 0.375$, with the experimental values, it has been found that the agreement is very poor.

Critical constants of gases

Gas	P_C (atm)	$V_{m,c}$ ($cm^3 mol^{-1}$)	T_C (K)
He	2.26	57.9	5.2
Ne	26.9	41.7	44.4
Ar	48.1	75.2	150.7
Xe	58.0	119.0	289.7
H_2	12.8	65.5	33.3
O_2	50.1	78.2	154.8
N_2	33.5	90.1	126.2
CO_2	72.8	94.0	304.2
H_2O	218.0	55.6	647.3
NH_3	111.5	72.5	405.0
CH_4	45.6	98.7	190.6
C_2H_6	48.2	148.0	305.4

Illustration 6:

The critical temperature and pressure of CO_2 gas are 304.2 K and 72.9 atm respectively. What is the radius of CO_2 molecule assuming it to behave as Vander Waal's gas ?

Solution:

$T_C = 304.2$ K $P_C = 72.9$ atm

$$T_C = \frac{8a}{27Rb} \qquad P_C = \frac{a}{27b^2}$$

$$\therefore \quad \frac{T_C}{P_C} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R} \qquad \text{or} \qquad b = \frac{RT_C}{8P_C} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277 \text{ lit mol}^{-1}$$

$$b = 4\,N_A \times \frac{4}{3}\pi r^3 = 42.77 \text{ cm}^3$$

or $r = (4.24)^{1/3} \times 10^{-8}$ cm $= 1.62 \times 10^{-8}$ cm

$\therefore$ radius of CO_2 molecule = 1.62 Å

The liquid state :

Liquid state is intermediate between gaseous and solid states. The liquids posses fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

The following general characteristics are exhibited by liquids :

(i) Shape :

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii) Volume :

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong.

(iii) Density :

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100° C and 1 atmospheric pressure is 0.958 g mL^{-1} while that of water vapour under similar conditions as calculated from ideal gas law $\left(d = \frac{MP}{RT}\right)$ is 0.000588 g mL^{-1}.

(iv) Compressibility :

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little on increasing pressure. Thus, liquids are relatively incompressible compared to gases.

(v) Diffusion :

When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small. Liquids diffuse slowly in comparison to gases.

(vi) Evaporation :

The process of changes of liquid into vapour state on standing is termed **evaporation**. Evaporation may be explained in terms of motion of molecules. At any given temperature all the motion of molecules does not possess the same kinetic energy (average kinetic energy is, however same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation depends on the following factor.

(a) Nature of the liquid : The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order :

Ether < Alcohol < Water

Alcohol < glycol < glycerol

$\longrightarrow$

Increasing extent of hydrogen bonding

(b) Surface area : Evaporation is a surface phenomenon. Larger the surface area, greater is the opportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

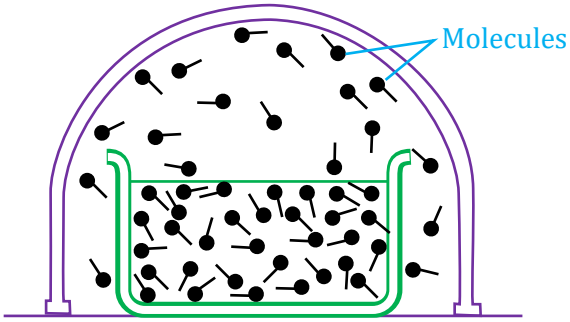
(c) Temperature : Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

(d) Flow of air current over the surface : Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation of liquid in open vessel.

(vii) Heat of vaporisation :

The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation. The heat of vaporisation depends on the strength of the intermolecular forces with in the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation**. It is numerically equal to the heat of vaporisation at the same temperature.

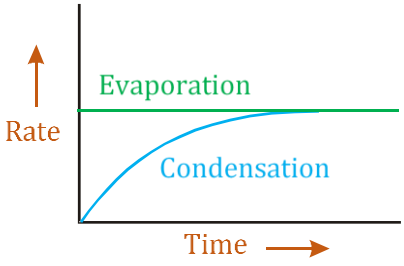
(viii) Vapour pressure :



When the space above the liquids is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they may be trapped. The return of the molecules from the vapour state of the liquid state is known as **condensation**. As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, i.e., the vapour in the closed container is in equilibrium with the liquid.

At equilibrium the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure**. Mathematically, it may be given by ideal gas equation, assuming ideal behaviour.



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

where C is the concentration of vapour, in mol/litre.

Since the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporisable liquids are called **volatile liquids** and they have relatively high vapour pressure. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table :

Substance	**Temperatures**				
	0° C	20° C	40° C	80° C	100° C
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	812.6	1693.3	
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

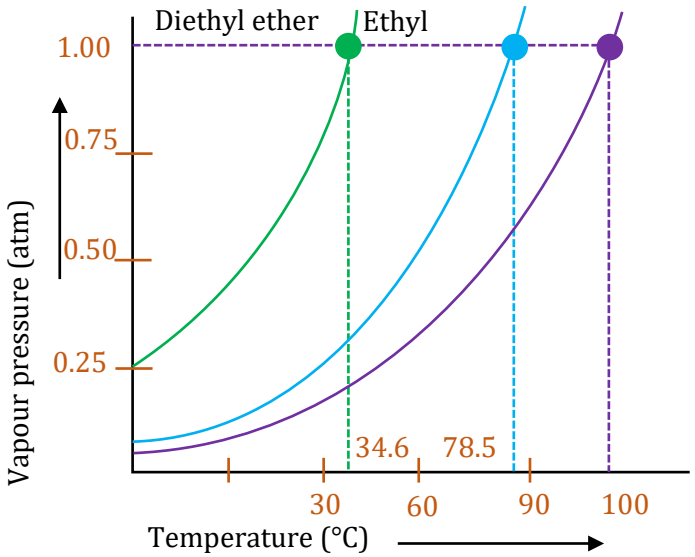
The vapour pressure of a given liquid at two different temperatures can be compared with the help of **Clausius-Clapeyron equation.**

$$\log\times\frac{P_2}{P_1}=\frac{\Delta H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Where ΔH is the latent heat of vaporisation and R is the molar gas constant.

(ix) Boiling point :

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling**. The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one atmospheric pressure (760 mm of Hg). Figure shows that normal boiling points of di-ethyl ether, ethyl alcohol and water are 34.6° C, 78.5° C and 100° C respectively.



The temperature of the liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintain the temperature because in the boiling process, the high energy molecules are lost by the liquid.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperatures higher than normal under external pressures greater than one atmosphere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperatures below its normal boiling water.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in following respects :

(a) Evaporation takes place spontaneously at all temperatures but boiling occurs at a particular temperature at which the vapour pressure is equal to the atmospheric pressure.

(b) Evaporation is surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

Note : Boiling does not occur when liquid is heated in a closed vessel.

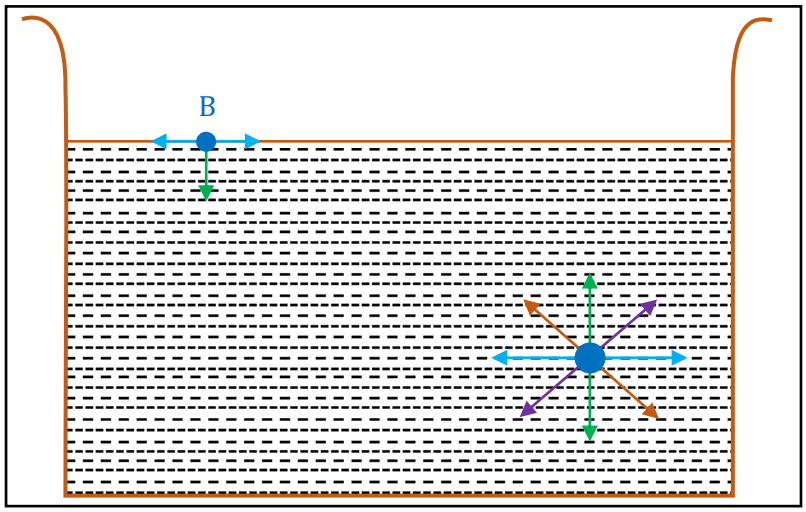
(x) Freezing point :

When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the rotational motion is seized. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point.**

Normal freezing point of a liquid is the temperature at which is liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point, which is called the **heat of fusion.**

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls. But the effect of pressures is very small because solid as well as liquid are almost incompressible.

(xi) Surface tension :



It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, i.e., are pulled inward and the surface area is minimized.

Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface. The unit of surface tension is dyne cm^{-1}. Surface tension is, thus, defined **as the force acting on the surface at right angles to any line of unit length.**

As the intermolecular forces of attraction decreases with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid may reduce its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

Many common phenomenon can be explained with the help of surface tension. Some are described here :

(a) Small droplets are spherical in shape :

The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

(b) Insects can walk on the surface of water :

Many insects can walk on the surface of water without drowing. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

(c) Cleaning action of soap and detergents :

Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d) Capillary action :

The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension.

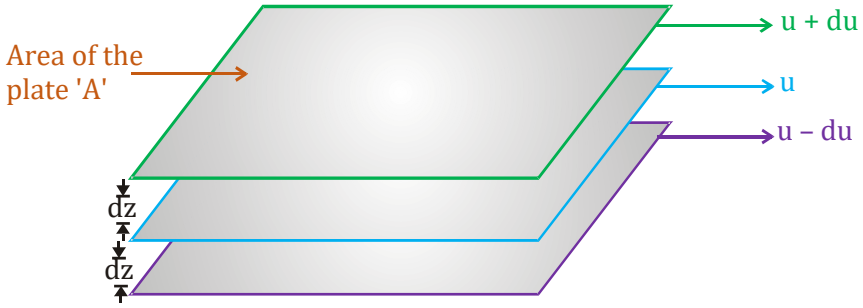
(e) Surface Energy :

The work required to be done to increase or extend surface area by unit area is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, i.e. J m^{-2} in S.I. system)

(xii) Viscosity :

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flow over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid, the layer above it accelerates its flow and the layer below this retards its flow.



Gradation of velocity in the laminar flow

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\frac{du}{dz}$. A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$F \alpha A$ (A is the area of contact)

$F \alpha A \frac{du}{dz}$ (where, $\frac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$F \alpha A. \frac{du}{dz} \Rightarrow F = \eta A \frac{du}{dz}$

'η' is proportionality constant and is called **coefficient of viscosity**. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'h' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre (N s m^{-2}) = pascal second (Pa s = 1kg $m^{-1}s^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise = 1 g $cm^{-1}s^{-1}$ = 10^{-1}kg $m^{-1}s^{-1}$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.