States of Matter- the Gaseuos State

The state of matter in which the molecular forces of attraction between the particles of matter are minimum, is known as *gaseous state*. It is the simplest state and shows great uniformity in behaviour.

Characteristics of gases.

(1) Gases or their mixtures are homogeneous in composition.

(2) Gases have very low density due to negligible intermolecular forces.

(3) Gases have *infinite expansibility and high compressibility*.

(4) Gases exert pressure.

(5) Gases possess high diffusibility.

(6) Gases do not have definite shape and volume like liquids.

(7) Gaseous molecules move very rapidly in all directions in a random manner *i.e.*, gases have highest kinetic energy.

(8) Gaseous molecules are loosely packed having large empty spaces between them.

(9) Gaseous molecules collide with one another and also with the walls of container with perfectly *elastic collisions*.

(10) Gases can be liquified, if subjected to low temperatures (below critical) or high pressures.

(11) Thermal energy of gases >> molecular attraction.

(12) Gases undergo similar change with the change of temperature and pressure. In other words, gases obey certain laws known as ***gas laws***.

Measurable properties of gases.

(1) The characteristics of gases are described fully in terms of four parameters or measurable properties :

(i) The volume, V, of the gas.

(ii) Its pressure, P

(iii) Its temperature, T

(iv) The amount of the gas (*i.e.*, mass or number of moles).

(2) **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 metres (m^3).

(iii) $1L = 1000\,mL$; $1\,mL = 10^{-3}\,L$

$$1L = 1\,dm^3 = 10^3\,cm^3$$

$$1\,m^3 = 10^3\,dm^3 = 10^6\,cm^3 = 10^6\,mL = 10^3\,L$$

(3) **Mass :** (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 weights gives the mass of the gas.

(ii) The mass of the gas is related to the number of moles of the gas *i.e.*

$$\text{moles of gas } (n) = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{m}{M}$$

(iii) Mass is expressed in grams or kilograms, $1\,Kg = 10^3\,g$

(4) **Temperature :** (i) Gases expand on increasing the temperature. If temperature is increased twice, the square of the velocity (v^2) also increases two times.

(ii) Temperature is measured in centigrade degree (^oC) or celsius degree with the help of thermometers. Temperature is also measured in Fahrenheit (F^o).

(iii) S.I. unit of temperature is kelvin (K) or absolute degree.

$$K = {}^oC + 273$$

(iv) Relation between F and ^oC is $\frac{^oC}{5} = \frac{F^o - 32}{9}$

(5) **Pressure :** (i) Pressure of the gas is the force exerted by the gas per unit area of the walls of the container in all directions. Thus, Pressure $(P) = \frac{\text{Force}(F)}{\text{Area}(A)} = \frac{\text{Mass}(m) \times \text{Acceleration}(a)}{\text{Area}(a)}$

(ii) Pressure exerted by a gas is due to kinetic energy ($KE = \frac{1}{2}mv^2$) of the molecules. Kinetic energy of the gas molecules increases, as the temperature is increased. Thus, ***Pressure of a gas*** $\propto$ ***Temperature (T)***.

(iii) Pressure of a pure gas is measured by manometer while that of a mixture of gases by barometer.

(iv) Commonly two types of manometers are used,

(a) Open end manometer; (b) Closed end manometer

(v) The S.I. unit of pressure, the pascal (Pa), is defined as 1 newton per *metre square*. It is very small unit.

$$1Pa = 1Nm^{-2} = 1kg\,m^{-1}s^{-2}$$

(vi) C.G.S. unit of pressure is dynes cm^{-2}.

(vii) M.K.S. unit of pressure is kgf/m^2. The unit kgf/cm^2 sometime called *ata* (atmosphere technical absolute).

(viii) Higher unit of pressure is *bar*, *KPa* or *MPa*.

$$1\,bar = 10^5\,Pa = 10^5\,Nm^{-2} = 100KNm^{-2} = 100KPa$$

(ix) Several other units used for pressure are,

Name	*Symbol*	*Value*
bar	**bar**	$1bar = 10^5 Pa$
atmosphere	**atm**	$1\,atm = 1.01325 \times 10^5\,Pa$
Torr	**Torr**	$1\,Torr = \frac{101325}{760}Pa = 133.322\,Pa$
millimetre of mercury	**mm Hg**	$1\,mm\,Hg = 133.322\,Pa$

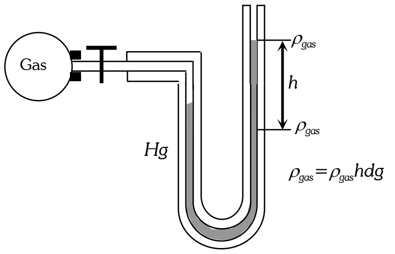
(x) The pressure relative to the atmosphere is called *gauge pressure*. The pressure relative to the perfect vacuum is called *absolute pressure*.

Absolute pressure = Gauge pressure + Atmosphere pressure.

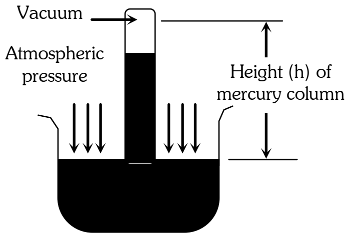
(xi) When the pressure in a system is less than atmospheric pressure, the gauge pressure becomes negative, but is frequently designated and called vacuum. For example, 16 *cm* vacuum will be

$$\frac{76-16}{76} \times 1.013 = 0.80\,bar\,.$$

(xii) If ‘h’ is the height of the fluid in a column or the difference in the heights of the fluid columns in the two limbs of the manometer d the density of the fluid $(Hg = 13.6 \times 10^3\ Kg/m^3 = 13.6\, g/cm^3)$ and g is the gravity, then pressure is given by, $P_{\text{gas}} = P_{\text{atm}} + hdg$



An open arm manometer



Mercury Barometer

(xiii) Two sets of conditions are widely used as 'standard' values for reporting data.

Condition	T	P	*V_m (Molar volume)*
S.T.P./N.T.P.	**273.15 K**	**1 atm**	**22.414 L**
S.A.T.P*.	**298.15 K**	**1 bar**	**24.800 L**

* Standard Ambient temperature and pressure.

Boyle's law.

(1) In 1662, ***Robert Boyle*** discovered the first of several relationships among gas variables (P, T, V).

(2) It states that, “*For a fixed amount of a gas at constant temperature, the gas volume is inversely proportional to the gas pressure.*”

Thus, $\boxed{P \propto \frac{1}{V}}$ at constant temperature and mass

or $P = \frac{K}{V}$ (where K is constant)

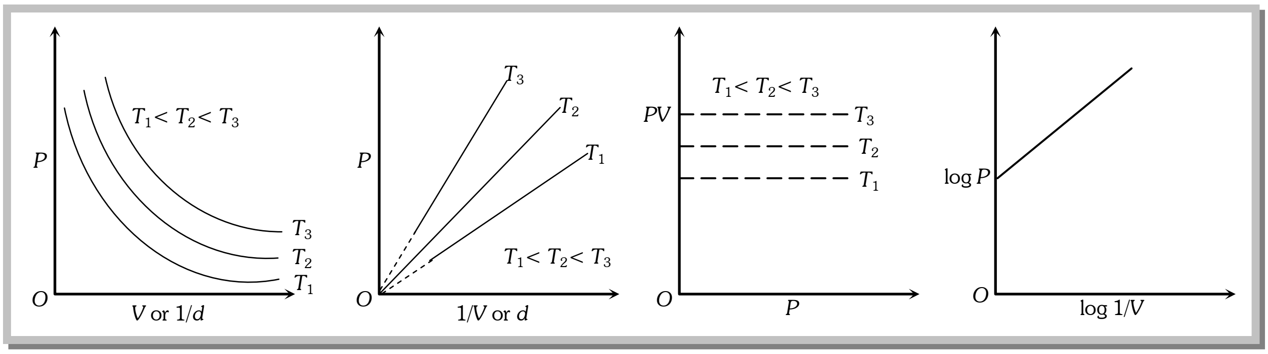
or $PV = K$

For two or more gases at constant temperature and mass.

$$P_1V_1 = P_2V_2 = ... = K$$

Boyle's law can also be given as, $\left(\frac{dP}{dV}\right)_T = -\frac{K}{v^2}$

(3) ***Graphical representation of Boyle's law :*** Graph between P and V at constant temperature is called ***isotherm*** and is an equilateral (or rectangular) hyperbola. By plotting P versus $\frac{1}{V}$, this hyperbola can be converted to a straight line. Other types of isotherms are also shown below,



Note : ✹ The isotherms of CO_2 were first studied by *Andrews*.

(4) At constant mass and temperature density of a gas is directly proportional to its pressure and inversely proportional to its volume.

Thus, $\boxed{d \propto P \propto \frac{1}{V}}$ $\left[\because V = \frac{\text{mass}}{d}\right]$

or $\boxed{\frac{d_1}{d_2} = \frac{P_1}{P_2} = \frac{V_2}{V_1} = ... = K}$

(5) At altitudes, as *P* is low *d* of air is less. That is why mountaineers carry oxygen cylinders.

(6) Air at the sea level is dense because it is compressed by the mass of air above it. However the density and pressure decreases with increase in altitude. The atmospheric pressure at Mount Everest is only 0.5 *atm*.

Example : 1 A sample of a given mass of a gas at a constant temperature occupies $95 cm^2$ under a pressure of $9.962 \times 10^4\ Nm^{-2}$. At the same temperature, it volume at a pressure of $10.13 \times 10^4\ Nm^{-2}$ is **[Bihar CEE 1992]**

(a) $190 cm^3$ (b) $93 cm^3$ (c) $46.5 cm^3$ (d) $47.5 cm^3$

Solution: (b) $P_1V_1 = P_2V_2$

$9.962 \times 10^4 \times 95 = 10.13 \times 10^4 \times V_2$

$V_2 = 93 cm^3$

Example : 2 A gas occupied a volume of 250 *ml* at 700 *mm Hg* pressure and $25^\circ C$. What additional pressure is required to reduce the gas volume to its 4/5th value at the same temperature

(a) 225 *mm Hg* (b) 175 *mm Hg* (c) 150 *mm Hg* (d) 265 *mm Hg*

Solution: (b) $P_1V_1 = P_2V_2$

$700 \times 250 = P_2 \times \left(\frac{4}{5} \times 250\right)$; $P_2 = 875 mm Hg$

Additional pressure required = 875 – 700 = 175 *mm Hg*

Example : 3 At constant temperature, if pressure increases by 1%, the percentage decrease of volume is

(a) 1% (b) 100/101% (c) 1/101% (d) 1/100%

Solution: (b) $P_1V_1 = P_2V_2$

If $P_1 = 100 mm$, P_2 will be 101 *mm*

Hence $100 \times V = 101 \times V_2$,

$V_2 = \frac{100}{101} \times V$,

Decrease in volume $= V - \frac{100V}{101} = \frac{1}{101}$ of V *i.e.* $\frac{100}{101}\%$

Charle's law.

(1) French chemist, ***Jacques Charles*** first studied variation of volume with temperature, in 1787.

(2) It states that, "*The volume of a given mass of a gas is directly proportional to the absolute temperature* $(= {}^{o}C + 273)$ *at constant pressure*".

Thus, $V \propto T$ at constant pressure and mass

or $V = KT = K(t({}^{o}C) + 273.15)$, (where k is constant),

$$\frac{V}{T} = K$$

For two or more gases at constant pressure and mass

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = ...K,$$

Charle's law can also be given as, $\left(\frac{dV}{dT}\right)_P = K$.

(3) If $t = 0^{o}C$, then $V = V_0$

hence, $V_0 = K \times 273.15$

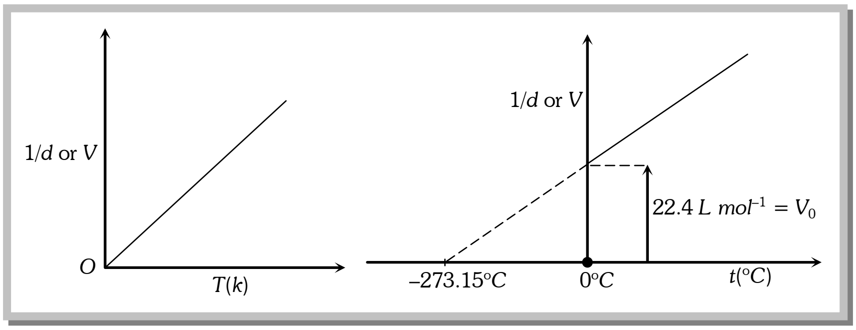
$$\therefore \quad K = \frac{V_0}{273.15}$$

$$V = \frac{V_0}{273.15}[t + 273.15] = V_0\left[1 + \frac{t}{273.15}\right] = V_0[1 + \alpha_v t]$$

where α_v is the volume coefficient, $\boxed{\alpha_v = \frac{V - V_0}{tV_0} = \frac{1}{273.15} = 3.661 \times 10^{-3}\ {}^{o}C^{-1}}$

Thus, for every 1^{o} change in temperature, the volume of a gas changes by $\frac{1}{273.15}\left(\approx \frac{1}{273}\right)$ of the volume at $0^{o}C$.

(4) ***Graphical representation of Charle's law*** **:** Graph between V and T at constant pressure is called *isobar or isoplestics* and is always a straight line. A plot of V versus $t({}^{o}C)$ at constant pressure is a straight line cutting the temperature axis at $-273.15^{o}C$. It is the lowest possible temperature.



(5) To lower the temperature of a substance, we reduce the thermal energy. Absolute zero (0*K*) is the temperature reached when all possible thermal energy has been removed from a substance. Obviously, a substance cannot be cooled any further after all thermal energy has been removed.

(6) At constant mass and pressure density of a gas is inversely proportional to it absolute temperature.

Thus, $\boxed{d \propto \frac{1}{T} \propto \frac{1}{V}}$ $\left[\because V = \frac{\text{mass}}{\text{d}}\right]$ or $\boxed{\frac{d_1}{d_2} = \frac{T_2}{T_1} = \frac{V_2}{V_1} = ... = K}$

(7) Use of hot air balloons in sports and meteorological observations is an application of Charle's law.

Example : 4 When the temperature of 23 *ml* of dry CO_2 gas is changed from 10^o to $30^o C$ at constant pressure of 760 *mm*, the volume of gas becomes closest to which one of the following **[CPMT 1992]**

(a) 7.7 *ml* (b) 25.5 *ml* (c) 24.6 *ml* (d) 69 *ml*

Solution: (c) $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ *i.e.* $\frac{23}{283\,K} = \frac{V_2}{303\,K}$; $V_2 = 24.6\,ml$

Example : 5 The volume of a gas is 100 *ml* at $100^o C$. If pressure remains constant then at what temperature it will be about 200 *ml* **[Roorkee 1993]**

(a) $200^o C$ (b) $473^o C$ (c) $746^o C$ (d) $50^o C$

Solution: (b) $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ *i.e.* $\frac{100}{373\,K} = \frac{200}{T_2}$

$T_2 = 746\,k = 473^o C$

Example : 6 If 300 *ml* of a gas at $27^o C$ is cooled to $7^o C$ at constant pressure, its final volume will be **[AIIMS 2000]**

(a) 135 *ml* (b) 540 *ml* (c) 350 *ml* (d) 280 *ml*

Solution: (d) $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ *i.e.* $\frac{300}{300\,K} = \frac{V_2}{280K}$

$V_2 = 280\,ml$

Example : 7 A flask containing air (open to atmosphere) is heated from 300 *K* to 500 *K*. the percentage of air escaped to the atmosphere is nearly **[CBSE PMT 1991]**

(a) 16.6 (b) 40 (c) 66 (d) 20

Solution: (c) $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ *i.e.* $\frac{V_1}{300} = \frac{V_2}{500}$; $V_2 = \frac{5}{3}V = 1.66\,V$

Volume escaped $= 1.66V - V = 0.66V = 66\%$ of V

Example : 8 According to Charle's law, at constant pressure, 100 ml of a given mass of a gas with $10^{o}C$ rise in temperature will become $\left(\frac{1}{273} = 0.00366\right)$

(a) 100.0366 (b) 99.9634 (c) 103.66 (d) 100.366

Solution: (a) $V_t = V_0 + \frac{V_0}{273} \times t = 100 + \frac{1}{273} \times 10 = 100 + 0.0366 = 100.0366\,ml$

Gay-Lussac's law (Amonton's law).

(1) In 1802, French chemist ***Joseph Gay-Lussac*** studied the variation of pressure with temperature and extende the Charle's law so, this law is also called Charle's-Gay Lussac's law.

(2) It states that, "*The pressure of a given mass of a gas is directly proportional to the absolute temperature* $(= {}^{o}C + 273)$ *at constant volume.*"

Thus, $P \propto T$ at constant volume and mass

or $P = KT = K(t({}^{o}C) + 273.15)$ (where K is constant)

$$\frac{P}{T} = K$$

For two or more gases at constant volume and mass

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

(3) If $t = 0^{o}C$, then $P = P_0$

Hence, $P_0 = K \times 273.15$

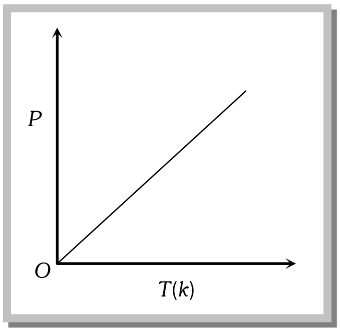
$$\therefore \quad K = \frac{P_0}{273.15}$$

$$P = \frac{P_0}{273.15}[t + 273.15] = P_0\left[1 + \frac{t}{273.15}\right] = P_0[1 + \alpha t]$$

where α_P is the pressure coefficient, $\boxed{\alpha_P = \frac{P - P_0}{tP_0} = \frac{1}{273.15} = 3.661 \times 10^{-3}\ {}^{o}C^{-1}}$

Thus, for every 1^{o} change in temperature, the pressure of a gas changes by $\frac{1}{273.15}\left(\approx \frac{1}{273}\right)$ of the pressure at $0^{o}C$.

(4) ***Graphical representation of Gay-Lussac's law :*** A graph between P and T at constant V is called ***isochore***.



Note : ✹ This law fails at low temperatures, because the volume of the gas molecules become significant.

Example : 9 A sealed tube which can withstand a pressure of 3 atmosphere is filled with air at $27^{o}C$ and 760 *mm* pressure. The temperature above which the tube will burst will be

(a) $900^{o}C$ (b) $627^{o}C$ (c) $627^{o}C$ (d) $1173^{o}C$

Solution: (b) The tube will burst when the final pressure exceeds 3 *atm.* at constant volume,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ i.e. } \frac{760}{300\,K} = \frac{3 \times 760}{T_2}$$

$$T_2 = 900\,K = 627^{o}C$$

Avogadro's law.

(1) According to this law, "*Equal volumes of any two gases at the same temperature and pressure contain the same number of molecules.*"

Thus, $V \propto n$ (at constant T and P)

or $V = Kn$ (where K is constant)

or $\frac{V_1}{n_1} = \frac{V_2}{n_2} = ... = K$

Example, $\underset{\begin{array}{c}2\,moles\\2\,volumes\\2\,litres\\1\,litre\\1\,n\,litre\end{array}}{2H_2(g)} + \underset{\begin{array}{c}1\,mole\\1\,volume\\1\,litre\\1/2\,litre\\1/2\,n\,litre\end{array}}{O_2(g)} \longrightarrow \underset{\begin{array}{c}2\,moles\\2\,volumes\\2\,litres\\1\,litre\\1\,n\,litre\end{array}}{2H_2O(g)}$

(2) One mole of any gas contains the same number of molecules (Avogadro's number $= 6.02 \times 10^{23}$) and by this law must occupy the same volume at a given temperature and pressure. The volume of one mole of a gas is called **molar volume, V_m** which is $22.4\,L\ mol^{-1}$ at S.T.P. or N.T.P.

(3) This law can also express as, "*The molar gas volume at a given temperature and pressure is a specific constant independent of the nature of the gas*".

Thus, $V_m =$ specific constant $= 22.4\,L\,mol^{-1}$ at S.T.P. or N.T.P.

(4) This law is widely applicable to solve the problems of reactive gaseous system.

Note : ✹ **Loschmidt number :** It is the number of molecules present in 1 *c.c.* of a gas or vapour at S.T.P. Its value is 2.687×10^{19} per *c.c.*

Ideal gas equation.

(1) The simple gas laws relating gas volume to pressure, temperature and amount of gas, respectively, are stated below :

Boyle's law :	$P \propto \frac{1}{V}$ or $V \propto \frac{1}{P}$	(n and T constant)
Charle's law :	$V \propto T$	(n and P constant)
Avogadro's law :	$V \propto n$	(T and P constant)

If all the above law's combines, then

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

or $$V = \frac{nRT}{P}$$

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

This is called ***ideal gas equation***. R is called ***ideal gas constant***. This equation is obeyed by isothermal and adiabatic processes.

(2) ***Nature and values of R :*** From the ideal gas equation, $R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{mole} \times \text{Temperature}}$

$$= \frac{\frac{\text{Force}}{\text{Area}} \times \text{Volume}}{\text{mole} \times \text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{mole} \times \text{Temperature}} = \frac{\text{Work or energy}}{\text{mole} \times \text{Temperature}}.$$

So, R is expressed in the unit of work or energy $mol^{-1}\,K^{-1}$.

Different values of R are summarised below :

$$R = 0.0821\, L\, atm\, mol^{-1}\, K^{-1}$$
$$= 8.3143 \times 10^{7}\, erg\, mol^{-1}\, K^{-1}$$
$$= 8.3143\, joule\, mol^{-1}\, K^{-1} \quad \text{(S.I. unit)}$$
$$= 8.3143\, Nm\, mol^{-1}\, K^{-1}$$
$$= 8.3143\, KPa\, dm^{3}\, mol^{-1}\, K^{-1}$$
$$= 8.3143\, MPa\, cm^{3}\, mol^{-1}\, K^{-1}$$
$$= 8.3143 \times 10^{-3}\, kJ\, mol^{-1}\, K^{-1}$$
$$= 5.189 \times 10^{19}\, eV\, mol^{-1}\, K^{-1}$$
$$= 1.99\, cal\, mol^{-1}\, K^{-1}$$
$$= 1.987 \times 10^{-3}\, K\, cal\, mol^{-1}\, K^{-1}$$

Note : ✸ Although R can be expressed in different units, but for pressure-volume calculations, R must be taken in the same units of pressure and volume.

(3) Gas constant, R for a single molecule is called *Boltzmann constant* (k)

$$k = \frac{R}{N} = \frac{8.314 \times 10^{7}}{6.023 \times 10^{23}}\, ergs\, mole^{-1}\, degree^{-1}$$

$$= 1.38 \times 10^{-16}\, ergs\, mol^{-1}\, degree^{-1} \text{ or } 1.38 \times 10^{-23}\, joule\, mol^{-1}\, degree^{-1}$$

(4) ***Calculation of mass, molecular weight and density of the gas by gas equation***

$$PV = nRT = \frac{m}{M}RT \qquad \left(\because n = \frac{\text{mass of the gas }(m)}{\text{Molecular weight of the gas }(M)}\right)$$

$$\therefore \boxed{M = \frac{mRT}{PV}}$$

$$\boxed{d = \frac{PM}{RT}} \qquad \left(\because d = \frac{m}{V}\right)$$

or $\frac{dT}{P} = \frac{M}{R}$

Since M and R are constant for a particular gas,

Thus, $\frac{dT}{P} = \text{constant}$

Thus, at two different temperature and pressure

$$\boxed{\frac{d_1T_1}{P_1} = \frac{d_2T_2}{P_2}}$$

(5) Gas densities differ from those of solids and liquids as,

(i) Gas densities are generally stated in g/L instead of g/cm^3.

(ii) Gas densities are strongly dependent on pressure and temperature as,

$$d \propto P$$

$$d \propto \frac{1}{T}$$

Densities of liquids and solids, do depend somewhat on temperature, but they are far less dependent on pressure.

(iii) The density of a gas is directly proportional to its molar mass. No simple relationship exists between the density and molar mass for liquid and solids.

(iv) Density of a gas at STP $= \frac{\text{molar mass}}{22.4}$

$$d(N_2) \text{ at STP} = \frac{28}{22.4} = 1.25\, g\, L^{-1}$$

$$d(O_2) \text{ at STP} = \frac{32}{22.4} = 1.43\, g\, L^{-1}$$

Example : 10 The pressure of 2 *moles* of an ideal gas at 546 *K* having volume 44.8 *L* is **[CPMT 1995]**

(a) 2 *atm* (b) 3 *atm* (c) 4 *atm* (d) 1 *atm*

Solution: (a) $PV = nRT, P \times 44.8 = 2 \times 0.082 \times 546$

$P = 2\, atm$

Example : 11 The number of moles of H_2 in 0.224 *litre* of hydrogen gas at STP (273 *K*, 1 *atm.*) is **[MLNR 1994]**

(a) 1 (b) 0.1 (c) 0.01 (d) 0.001

Solution: (c) $PV = nRT$, $1 \times 0.224 = n \times 0.082 \times 273$ $n = 0.01 mol$

Example : 12 120 *g* of an ideal gas of molecular weight 40 $mole^{-1}$ are confined to a volume of 20 *L* at 400 *K*. Using $R = 0.0821\, L\, atm\, K^{-1}\, mole^{-1}$, the pressure of the gas is **[Pb. CET 1996]**

(a) 4.90 *atm* (b) 4.92 *atm* (c) 5.02 *atm* (d) 4.96 *atm*

Solution: (b) $120\,g = \frac{120}{40} = 3\,moles$

$$P = \frac{nRT}{V} = \frac{3 \times 0.0821 \times 400}{20} = 4.92\,atm.$$

Example : 13 The volume of 2.8 *g* of carbon monoxide at $27^o C$ and 0.821 *atm* pressure is $(R = 0.0821\,lit\,atm\,K^{-1}\,mol^{-1})$ **[Manipal PMT 2001]**

(a) 0.3 *litre* (b) 1.5 *litre* (c) 3 *litre* (d) 30 *litre*

Solution: (c) $2.8\,g\,CO = \frac{2.8}{28} = mol = 0.1\,mol$

$$PV = nRT$$

or $V = \frac{nRT}{P} = \frac{0.1 \times 0.0821 \times 300}{0.821} = 3\,litre$

Example: 14 3.2 *g* of oxygen (At. wt. = 16) and 0.2 *g* of hydrogen (At. wt. = 1) are placed in a 1.12 *litre* flask at $0^o C$. The total pressure of the gas mixture will be **[CBSE PMT 1992]**

(a) 1 *atm* (b) 4 *atm* (c) 3 *atm* (d) 2 *atm*

Solution: (b) $3.2\,g\;O_2 = 0.1\,mol$, $0.2\,g\,H_2 = 0.1\,mol,$

Total $n = 0.2\,mol$,

$$P = \frac{nRT}{V} = \frac{0.2 \times 0.082 \times 273}{1.12} = 4 atm$$

Example : 15 The density of methane at 2.0 atmosphere pressure and $27^o C$ is **[BHU 1994]**

(a) $0.13\,g\,L^{-1}$ (b) $0.26\,g\,L^{-1}$ (c) $1.30\,g\,L^{-1}$ (d) $2.60\,g\,L^{-1}$

Solution: (c) $d = \frac{PM}{RT} = \frac{2 \times 16}{0.082 \times 300} = 1.30\,g\,L^{-1}$

Example : 16 The volume of 0.0168 *mol* of O_2 obtained by decomposition of $KClO_3$ and collected by displacement of water is 428 *ml* at a pressure of 754 *mm Hg* at $25^o C$. The pressure of water vapour at $25^o C$ is **[UPSEAT 1996]**

(a) 18 *mm Hg* (b) 20 *mm Hg* (c) 22 *mm Hg* (d) 24 *mm Hg*

Solution: (d) Volume of 0.0168 *mol* of O_2 at STP $= 0.0168 \times 22400\,cc = 376.3\,cc$

$V_1 = 376.3\,cc$, $P_1 = 760\,mm$, $T_1 = 273\,K$

$V_2 = 428\,cc$, $P_2 = ?$, $T_2 = 298\,K$

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ gives $P_2 = 730\,mm$ (approx.)

$\therefore$ Pressure of water vapour $= 754 - 730 = 24$ *mm Hg*

Dalton's law of partial pressures.

(1) According to this law, "*When two or more gases, which do not react chemically are kept in a closed vessel, the total pressure exerted by the mixture is equal to the sum of the partial pressures of individual gases.*"

Thus, $P_{\text{total}} = P_1 + P_2 + P_3 + ...$

Where $P_1, P_2, P_3, ...$ are partial pressures of gas number 1, 2, 3 ....

(2) ***Partial pressure*** is the pressure exerted by a gas when it is present alone in the same container and at the same temperature.

$$\text{Partial pressure of a gas } (P_1) = \frac{\text{Number of moles of the gas } (n_1) \times P_{\text{Total}}}{\text{Total number of moles } (n) \text{ in the mixture}} = \text{Mole fraction } (X_1) \times P_{\text{Total}}$$

(3) If a number of gases having volume $V_1, V_2, V_3......$ at pressure $P_1, P_2, P_3........$ are mixed together in container of volume V, then,

$$P_{\text{Total}} = \frac{P_1V_1 + P_2V_2 + P_3V_3.....}{V}$$

$$\text{or } = (n_1 + n_2 + n_3.....)\frac{RT}{V} \quad (\because PV = nRT) \quad \text{or } = n\frac{RT}{V} \quad (\because n = n_1 + n_2 + n_3.....)$$

(4) ***Applications*** **:** This law is used in the calculation of following relationships,

(i) Mole fraction of a gas (X_1) in a mixture of gas $= \dfrac{\text{Partial pressure of a gas } (P_1)}{P_{\text{Total}}}$

(ii) % of a gas in mixture $= \dfrac{\text{Partial pressure of a gas } (P_1)}{P_{\text{Total}}} \times 100$

(iii) Pressure of dry gas collected over water : When a gas is collected over water, it becomes moist due to water vapour which exerts its own partial pressure at the same temperature of the gas. *This partial perssure of water vapours is called aqueous tension.* Thus,

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

or $P_{\text{dry gas}} = P_{\text{moist gas}}$ – Aqueous tension (Aqueous tension is directly proportional to absolute temperature)

(iv) Relative humidity (RH) at a given temperature is given by :

$$RH = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}.$$

(5) ***Limitations*** **:** This law is applicable only when the component gases in the mixture do not react with each other. For example, N_2 and O_2, CO and CO_2, N_2 and Cl_2, CO and N_2 etc. But this law is not applicable to gases which combine chemically. For example, H_2 and Cl_2, CO and Cl_2, NH_3, HBr and HCl, NO and O_2 etc.

Note : ✹ N_2 (80%) has the highest partial pressure in atmosphere.

(6) Another law, which is really equivalent to the law of partial pressures and related to the partial volumes of gases is known as *Law of partial volumes* given by Amagat. According to this law, "*When two or more gases, which do not react chemically are kept in a closed vessel, the total volume exerted by the mixture is equal to the sum of the partial volumes of individual gases.*"

Thus, $V_{\text{Total}} = V_1 + V_2 + V_3 + ...$

Where $V_1, V_2, V_3,......$ are partial volumes of gas number 1, 2, 3.....

Example: 17 What will be the partial pressure of H_2 in a flask containing 2 g of H_2, 14 g of N_2 and 16 g of O_2

[Assam JET 1992]

(a) 1/2 the total pressure (b) 1/3 the total pressure (c) 1/4 the total pressure (d) 1/16 the total pressure

Solution: (a) $n(H_2) = \frac{2}{2} = 1, n(N_2) = \frac{14}{28} = 0.5$, $n(O_2) = \frac{16}{32} = 0.5, p(H_2) = \frac{1}{1 + 0.5 + 0.5}p = \frac{1}{2}p$

Example : 18 Equal weights of methane and oxygen are mixed in an empty container at $25^o C$. The fraction of the total pressure exerted by oxygen is **[IIT 1981]**

(a) 1/3 (b) 1/2 (c) 2/3 (d) $1/3 \times 273/298$

Solution: (a) $n(CH_4) = \frac{w}{16} = 1, n(O_2) = \frac{w}{32}$

$$p(O_2) = \frac{w/32}{w/16 + w/32} = \frac{1}{2+1} = \frac{1}{3}$$

Example : 19 In a flask of volume *V litres*, 0.2 *mol* of oxygen, 0.4 *mol* of nitrogen, 0.1 *mol* of ammonia and 0.3 *mol* of helium are enclosed at $27^o C$. If the total pressure exerted by these non-reating gases is one atmosphere, the partial pressure exerted by nitrogen is **[Kerala MEE 2001]**

(a) 1 *atm* (b) 0.1 *atm* (c) 0.2 *atm* (d) 0.4 *atm*

Solution: (d) $P_{N_2} = \text{Mol. fraction of } N_2 \times \text{Total perssure} = \frac{0.4}{0.2+0.4+0.1+0.3} \times 1\,atm = 0.4\,atm$.

Example : 20 Equal weights of ethane and hydrogen are mixed in an empty container at $25^o C$. The fraction of the total pressure exerted by hydrogen is **[IIT 1993]**

(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16

Solution: (d) $n(C_2H_6) = \frac{w}{30}, n(H_2) = \frac{w}{2}$

$$p(H_2) = \frac{w/2}{w/2 + w/30} = \frac{1}{1 + \frac{1}{15}} = \frac{15}{16}$$

Example : 21 A gaseous mixture contains 56 *g* of N_2, 44 *g* of CO_2 and 16 *g* of CH_4. The total pressure of the mixture is 720 *mm Hg*. The partial pressure of CH_4 is **[IIT 1993]**

(a) 180 *mm* (b) 360 *mm* (c) 540 *mm* (d) 720 *mm*

Solution: (a) $p(CH_4) = \frac{16/16}{5/28 + 44/44 + 16/16} \times 720 = \frac{1}{2+1+1} \times 720 = \frac{1}{4} \times 720 = 180\,mm$.

Graham's law of diffusion and effusion.

(1) ***Diffusion*** is the process of spontaneous spreading and intermixing of gases to form homogenous mixture irrespective of force of gravity. While ***Effusion*** is the escape of gas molecules through a tiny hole such as pinhole in a balloon.

- All gases spontaneously diffuse into one another when they are brought into contact.
- Diffusion into a vacuum will take place much more rapidly than diffusion into another place.
- Both the rate of diffusion of a gas and its rate of effusion depend on its molar mass. Lighter gases diffuses faster than heavier gases. The gas with highest rate of diffusion is *hydrogen*.

(2) According to this law, "*At constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its vapour density.*"

Thus, rate of diffusion $(r) \propto \frac{1}{\sqrt{d}}$ (T and P constant)

For two or more gases at constant pressure and temperature,

$$\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}$$

Note : ✹ Always remember that vapour density is different from absolute density. The farmer is independent of temperature and has no unit while the latter depends upon temperature and expressed in gm^{-1}.

(3) Graham's law can be modified in a number of ways as,

(i) Since, 2 × vapour density (V.D.) = Molecular weight

then, $\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}=\sqrt{\frac{d_2\times 2}{d_1\times 2}}=\sqrt{\frac{M_2}{M_1}}$

where, M_1 and M_2 are the molecular weights of the two gases.

(ii) Since, rate of diffusion $(r)=\frac{\text{Volume of a gas diffused}}{\text{Time taken for diffusion}}$

then, $\frac{r_1}{r_2}=\frac{V_1/t_1}{V_2/t_2}=\sqrt{\frac{d_2}{d_1}}$

(a) When equal volume of the two gases diffuse, *i.e.* $V_1=V_2$

then, $\frac{r_1}{r_2}=\frac{t_2}{t_1}=\sqrt{\frac{d_2}{d_1}}$

(b) When volumes of the two gases diffuse in the same time, *i.e.* $t_1=t_2$

then, $\frac{r_1}{r_2}=\frac{V_1}{V_2}=\sqrt{\frac{d_2}{d_1}}$

(iii) Since, $r\propto p$ (when *p* is not constant)

then, $\frac{r_1}{r_2}=\frac{P_1}{P_2}=\sqrt{\frac{M_2}{M_1}}\quad\left(\because r\propto\frac{1}{\sqrt{M}}\right)$

Note : ✹ It should be noted that this law is true only for gases diffusing under low pressure gradient.

✹ $CO_2>SO_2>SO_3>PCl_3$ is order of rates of diffusion.

(4) Rate of diffusion and effusion can be determined as,

(i) Rate of diffusion is equal to distance travelled by gas per unit time through a tube of uniform cross-section.

(ii) Number of moles effusing per unit time is also called rate of diffusion.

(iii) Decrease in pressure of a cylinder per unit time is called rate of effusion of gas.

(iv) The volume of gas effused through a given surface per unit time is also called rate of effusion.

(5) ***Applications*** **:** Graham's law has been used as follows :

(i) To determine vapour densities and molecular weights of gases.

(ii) To prepare Ausell's marsh gas indicator, used in mines.

(iii) ***Atmolysis*** **:** The process of separation of two gases on the basis of their different rates of diffusion due to difference in their densities is called atmolysis. It has been applied with success for the separation of isotopes and other gaseous mixtures. Example, this process was used for the large-scale separation of gaseous $^{235}UF_6$ and $^{238}UF_6$ during the second world war.

Example : 22 The time taken for a certain volume of a gas 'X' to diffuse through a small hole is 2 minutes. It takes 5.65 minutes for oxygen to diffuse under the similar conditions. The molecular weight of 'X' is **[NCERT 1990]**

(a) 8 (b) 4 (c) 16 (d) 32

Solution: (b) $\frac{r_X}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_X}}$

$$\frac{\upsilon/2}{\upsilon/5.65} = \sqrt{\frac{32}{M_X}}, \frac{5.65}{2} = \sqrt{\frac{32}{M_X}}, M_X = 4$$

Example : 23 The rate of diffusion of methane at a given temperature is twice that of gas X. The molecular weight of X is **[IIT 1990]**

(a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0

Solution: (a) $\frac{r_{CH_4}}{r_X} = \sqrt{\frac{M_X}{M_{CH_4}}} \Rightarrow 2 = \sqrt{\frac{M_X}{16}} \Rightarrow M_X = 64$.

Example : 24 Density ratio of O_2 and H_2 is 16 : 1. The ratio of their r.m.s. velocities will be **[AIIMS 2000]**

(a) 4 : 1 (b) 1 : 16 (c) 1 : 4 (d) 16 : 1

Solution: (c) $\frac{r_1}{r_2} = \frac{\upsilon_1}{\upsilon_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{1}{16}} = 1:4$.

Example : 25 The rate of diffusion of a gas having molecular weight just double of nitrogen gas is 56 $ml\,s^{-1}$. The rate of diffusion of nitrogen will be **[CPMT 2000]**

(a) 79.19 $ml\,s^{-1}$ (b) 112.0 $ml\,s^{-1}$ (c) 56 $ml\,s^{-1}$ (d) 90.0 $ml\,s^{-1}$

Solution: (a) $\frac{r_X}{r_{N_2}} = \sqrt{\frac{M_{N_2}}{M_X}} = \sqrt{\frac{28}{56}} = \sqrt{\frac{1}{2}}$; $\frac{56}{r_{N_2}} = \frac{1}{\sqrt{2}}$ or $r_{N_2} = 56\sqrt{2} = 79.19\,ms^{-1}$

Example : 26 50 *ml* of gas *A* diffuse through a membrane in the same time as 40 *ml* of a gas *B* under identical pressure-temperature conditions. If the molecular weight of *A* is 64, that of *B* would be **[CBSE PMT 1992]**

(a) 100 (b) 250 (c) 200 (d) 80

Solution: (a) $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{50/t}{40/t} = \sqrt{\frac{M_2}{64}}$

$$\frac{50}{40} = \sqrt{\frac{M_2}{64}} \text{ or } \frac{5}{4} = \sqrt{\frac{M_2}{64}} \text{ or } \frac{25}{16} = \frac{M_2}{64} \text{ or } M_2 = 100$$

Barometric distribution law.

(1) For gaseous systems, gravitational force is negligible but this is not true for the gases of high molecular masses such as polymer. In this case, the pressure will be different in vertical positions in a container. The variation of pressure with altitude is given by the so-called *Barometric formula*.

$$\boxed{P = P^o e^{-Mgh/RT}}$$

where, P^o and P are the pressure of the gas at the ground level and at a height 'h' from the ground respectively. M is molecular mass of the gas, g is acceleration due to gravity, R is gas constant and T is temperature in *kelvin*.

(2) Since number of moles of gas 'n' and density of the gas 'd' are directly proportional to pressure hence the above equation may be expressed as, $d = d^o e^{-Mgh/RT}$ and $n = n^o e^{-Mgh/RT}$.

(3) The above equations may be expressed as,

$$\boxed{\log\frac{P}{P^o} = \log\frac{d}{d^o} = \log\frac{n}{n^o} = -\frac{1}{2.303}\times\frac{Mgh}{RT}}$$

Kinetic theory of gases.

(1) Kinetic theory was developed by Bernoulli, Joule, Clausius, Maxwell and Boltzmann etc. and represents ***dynamic particle or microscopic model*** for different gases since it throws light on the behaviour of the particles (atoms and molecules) which constitute the gases and cannot be seen. Properties of gases which we studied earlier are part of macroscopic model.

(2) ***Postulates***

(i) Every gas consists of a large number of small particles called molecules moving with very high velocities in all possible directions.

(ii) The volume of the individual molecule is negligible as compared to the total volume of the gas.

(iii) Gaseous molecules are *perfectly elastic* so that there is no net loss of kinetic energy due to their collisions.

(iv) The effect of gravity on the motion of the molecules is negligible.

(v) Gaseous molecules are considered as *point masses* because they do not posses potential energy. So the attractive and repulsive forces between the gas molecules are negligible.

(vi) The pressure of a gas is due to the continuous bombardment on the walls of the containing vessel.

(vii) At constant temperature the average K.E. of all gases is same.

(viii) The average K.E. of the gas molecules is directly proportional to the absolute temperature.

(3) ***Kinetic gas equation :*** On the basis of above postulates, the following gas equation was derived,

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

where, P = pressure exerted by the gas, V = volume of the gas, m = average mass of each molecule, n = number of molecules, u = root mean square (RMS) velocity of the gas.

(4) ***Calculation of kinetic energy***

We know that,

$$\text{K.E. of one molecule} = \frac{1}{2}mu^2$$

$$\text{K.E. of } n \text{ molecules} = \frac{1}{2}mnu^2 = \frac{3}{2}PV \quad (\because\ PV = \frac{1}{3}mnu^2)$$

$n = 1$, Then K.E. of 1 mole gas $= \frac{3}{2}RT \qquad (\because PV = RT)$

$$= \frac{3}{2} \times 8.314 \times T = 12.47\, T\, Joules.$$

$$= \frac{\text{Average K.E. per mole}}{N(\text{Avogadro number})} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}KT \quad \left(K = \frac{R}{N} = \text{Boltzmann constant}\right)$$

This equation shows that K.E. of translation of a gas depends only on the absolute temperature. This is known as *Maxwell generalisation*. Thus average K.E. $\propto T$.

If $T = 0K$ (*i.e.*, $-273.15^{o}C$) then, average K.E. $= 0$. Thus, absolute zero ($0K$) is the temperature at which molecular motion ceases.

(5) Kinetic gas equation can be used to establish gas laws.

Example : 27 The kinetic energy for 14 *grams* of nitrogen gas at $127^{o}C$ is nearly (mol. mass of nitrogen = 28 and gas constant = $8.31\, JK^{-1}\, mol^{-1}$) **[CBSE PMT 1999]**

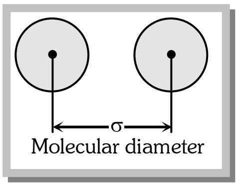
(a) $1.0\,J$ (b) $4.15\,J$ (c) $2493\,J$ (d) $3.3\,J$

Solution: (c) K.E. $= \frac{3}{2}RT\, mol^{-1}$

or K.E. $= \frac{3}{2}nRT = \frac{3}{2} \times \frac{14}{28} \times 8.31 \times 400\, J = 2493\, J$

Molecular collisions.

(1) The closest distance between the centres of two molecules taking part in a collision is called *molecular or collision diameter* (σ). The molecular diameter of all the gases is nearly same lying in the order of $10^{-8}\, cm$.



(2) The number of collisions taking place in unit time per unit volume, called *collision frequency* (z).

(i) The number of collision made by a single molecule with other molecules per unit time are given by,

$$Z_A = \sqrt{2}\pi\sigma^2 u_{\text{av.}} n$$

where n is the number of molecules per unit molar volume,

$$n = \frac{\text{Avogadro number}(N_0)}{V_m} = \frac{6.02 \times 10^{23}}{0.0224} m^{-3}$$

(ii) The total number of bimolecular collision per unit time are given by,

$$Z_{AA} = \frac{1}{\sqrt{2}}\pi\sigma^2 u_{\text{av.}} n^2$$

(iii) If the collisions involve two unlike molecules, the number of bimolecular collision are given by,

$$Z_{AB} = \sigma_{AB}^2 \left[8\pi RT \frac{(M_A + M_B)}{M_A M_B} \right]^{1/2}$$

where, $\sigma_{AB} = \dfrac{\sigma_A + \sigma_B}{2}$ and M_A, M_B are molecular weights $(M = mN_0)$

(iv) (a) At particular temperature; $Z \propto p^2$

(b) At particular pressure; $Z \propto T^{-3/2}$

(c) At particular volume; $Z \propto T^{1/2}$

(3) During molecular collisions a molecule covers a small distance before it gets deflected. *The average distance travelled by the gas molecules between two successive collision is called mean free path (λ).*

$$\lambda = \frac{\text{Average distance travelled per unit time}(u_{av})}{\text{No. of collisions made by single molecule per unit time }(Z_A)} = \frac{u_{av}}{\sqrt{2}\pi\sigma^2 u_{avr.} n} = \frac{1}{\sqrt{2}\pi n \sigma^2}.$$

(4) Based on kinetic theory of gases mean free path, $\lambda \propto \dfrac{T}{P}$. Thus,

(i) Larger the size of the molecules, smaller the mean free path, *i.e.*, $\lambda \propto \dfrac{1}{(\text{radius})^2}$

(ii) Greater the number of molecules per unit volume, smaller the mean free path.

(iii) Larger the temperature, larger the mean free path.

(iv) Larger the pressure, smaller the mean free path.

(5) Relation between collision frequency (Z) and mean free path (λ) is given by,

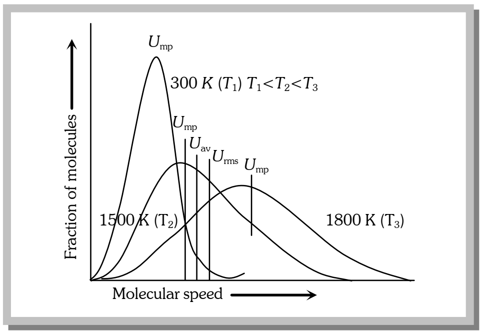
$$\boxed{Z = \frac{u_{rms}}{\lambda}}$$

Molecular speeds or velocities.

(1) At any particular time, in the given sample of gas all the molecules do not possess same speed, due to the frequent molecular collisions with the walls of the container and also with one another, the molecules move with ever changing speeds and also with ever changing direction of motion.

(2) According to Maxwell, at a particular temperature the distribution of speeds remains constant and this distribution is referred to as the *Maxwell-Boltzmann distribution* and given by the following expression,

$$\frac{dn_0}{n} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} .e^{-Mu^2/2RT} .u^2 dc$$



where, dn_0 = Number of molecules out of total number of molecules n, having velocities between c and $c + dc$, dn_0 / n = Fraction of the total number of molecules, M = molecular weight, T = absolute temperature. The exponential factor $e^{-Mu^2/2RT}$ is called *Boltzmann factor*.

(3) Maxwell gave distribution curves of molecular speeds for CO_2 at

different temperatures. Special features of the curve are :

(i) Fraction of molecules with two high or two low speeds is very small.

(ii) No molecules has zero velocity.

(iii) Initially the fraction of molecules increases in velocity till the peak of the curve which pertains to most probable velocity and thereafter it falls with increase in velocity.

(4) **Types of molecular speeds or Velocities :**

(i) **Root mean square velocity** (u_{rms}) **:** It is the square root of the mean of the squares of the velocity of a large number of molecules of the same gas.

$$u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + ...u_n^2}{n}}$$

$$u_{rms} = \sqrt{\frac{3PV}{(mN_0) = M}} = \sqrt{\frac{3RT}{(mN_0) = M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3P}{d}}$$

where k = Boltzmann constant $= \frac{R}{N_0}$

(a) For the same gas at two different temperatures, the ratio of RMS velocities will be, $\frac{u_1}{u_2} = \sqrt{\frac{T_1}{T_2}}$

(b) For two different gases at the same temperature, the ratio of RMS velocities will be, $\frac{u_1}{u_2} = \sqrt{\frac{M_2}{M_1}}$

(c) RMS velocity at any temperature $t^\circ C$ may be related to its value at S.T.P. as, $u_t = \sqrt{\frac{3P(273+t)}{273d}}$.

Note : ✸ RMS velocity explained the non-existence of gases in the atmosphere of moon.

✸When temperature alone is given then, $u_{rms} = 1.58 \times \sqrt{\frac{T}{M}} \times 10^4 \, cm/\sec$.

✸If P and T both are given, use equation in terms of temperature, *i.e.*, use $u_{rms} = \sqrt{\frac{3RT}{M}}$ and not $\sqrt{\frac{3PV}{M}}$

(ii) **Average velocity** (v_{av}) : It is the average of the various velocities possessed by the molecules.

$$v_{av} = \frac{v_1 + v_2 + v_3 + ...v_n}{n}$$

$$v_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

(iii) **Most probable velocity** (α_{mp}) **:** It is the velocity possessed by maximum number of molecules of a gas at a given temperature.

$$\alpha_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{d}}$$

(5) **Relation between molecular speeds or velocities,**

(i) Relation between u_{rms} and v_{av}: $v_{av} = 0.9213 \times u_{rms}$ or $u_{rms} = 1.085 \times v_{av}$

(ii) Relation between α_{mp} and u_{rms}: $\alpha_{mp} = 0.816 \times u_{rms}$ or $u_{rms} = 1.224 \times \alpha_{mp}$

(iii) Relation between α_{mp} and v_{av}: $v_{av} = 1.128 \times \alpha_{mp}$

(iv) Relation between α_{mp}, v_{av} and u_{rms}:

$$\begin{array}{lllll}
\alpha_{mp} & : & v_{av} & : & u_{rms} \\
\sqrt{\dfrac{2RT}{M}} & : & \sqrt{\dfrac{8RT}{\pi M}} & : & \sqrt{\dfrac{3RT}{M}} \\
\sqrt{2} & : & \sqrt{\dfrac{8}{\pi}} & : & \sqrt{3} \\
1.414 & : & 1.595 & : & 1.732 \\
1 & : & 1.128 & : & 1.224 \quad i.e., \ \alpha_{mp} < v_{av} < u_{rms}
\end{array}$$

Example : 28 The *rms* velocity of CO_2 at a temperature T (in *kelvin*) is $x \; cm \, s^{-1}$. At what temperature (in *kelvin*) the *rms* velocity of nitrous oxide would be $4x \; cm \, s^{-1}$ **[EAMCET 2001]**

(a) $16\,T$ (b) $2\,T$ (c) $4\,T$ (d) $32\,T$

Solution: (a) $u = \sqrt{\dfrac{3RT}{M}}$

$$\therefore \quad \frac{u_{CO_2}}{u_{N_2O}} = \sqrt{\frac{T_{CO_2}}{M_{CO_2}} \times \frac{M_{N_2O}}{T_{N_2O}}}$$

$$i.e., \ \frac{x}{4x} = \sqrt{\frac{T}{44} \times \frac{44}{T_{N_2O}}} \ \text{ or } \ \frac{1}{4} = \sqrt{\frac{T}{T_{N_2O}}} \ \text{ or } \ T_{N_2O} = 16\,T$$

Example : 29 The *rms* velocity of an ideal gas at 27^oC is 0.3 ms^{-1}. Its *rms* velocity at 927^oC (in ms^{-1}) is **[IIT 1996; EAMCET 1991]**

(a) 3.0 (b) 2.4 (c) 0.9 (d) 0.6

Solution: (d) $u = \sqrt{\dfrac{3RT}{M}}$

For the same gas at two different temperatures,

$$\frac{u_1}{u_2} = \sqrt{\frac{T_1}{T_2}}; \quad \frac{0.3}{u_2} = \sqrt{\frac{300}{1200}} = \frac{1}{2}, \ u_2 = 0.6\,ms^{-1}$$

Example : 30 The *rms* velocity of hydrogen is $\sqrt{7}$ times the *rms* velocity of nitrogen. If T is the temperature of the gas **[IIT 2000]**

(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$ (c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\,T(N_2)$

Solution: (c) $u=\sqrt{\frac{3RT}{M}}$; $\therefore \frac{u(H_2)}{u(N_2)}=\sqrt{\frac{T(H_2)}{M(H_2)}\times\frac{M(N_2)}{T(N_2)}}$ or $\sqrt{7}=\sqrt{\frac{T(H_2)}{T(N_2)}\times\frac{28}{2}}$ or $7=\frac{T(H_2)}{T(N_2)}\times 14$ or $\frac{T(H_2)}{T(N_2)}=\frac{1}{2}$

or $T(N_2)=2\times T(H_2)$ *i.e.*, $T(N_2)>T(H_2)$

Example : 31 If the average velocity of N_2 molecules is 0.3 *m/s* at 27^oC, then the velocity of 0.6 *m/s* will take place at **[Manipal PMT 2001]**

(a) 273 *K* (b) 927 *K* (c) 1000 *K* (d) 1200 *K*

Solution: (d) $v=0.921u$

$$\therefore \quad \frac{v_1}{v_2}=\frac{u_1}{u_2}=\sqrt{\frac{T_1}{T_2}}$$

$$\therefore \quad \frac{0.3}{0.6}=\sqrt{\frac{300}{T_2}} \text{ or } \frac{1}{2}=\sqrt{\frac{300}{T_2}} \text{ or } T_2=300\times 4=1200\,K$$

Example : 32 The temperature of an ideal gas is reduced from 927^oC to 27^oC. The *rms* velocity of the molecules becomes **[Kerala CEE 2001]**

(a) Double the initial value (b) Half of the initial value

(c) Four times the initial value (d) Ten times the initial value

Solution: (b) $u=\sqrt{\frac{3RT}{M}}$

$$\therefore \quad \frac{u_1}{u_2}=\sqrt{\frac{T_1}{T_2}}=\sqrt{\frac{927+273}{27+273}}=\sqrt{\frac{1200}{300}}=\sqrt{4}=2$$

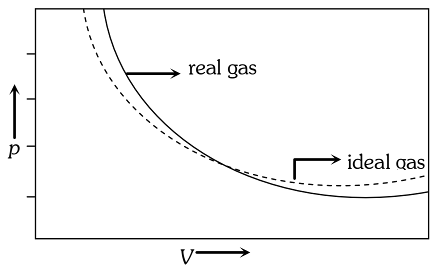
$$\therefore u_2=\frac{1}{2}u_1$$

Real and ideal gases.

(1) Gases which obey gas laws or ideal gas equation $(PV=nRT)$ at all temperatures and pressures are called *ideal or perfect gases.* Almost all gases deviate from the ideal behaviour *i.e., no gas is perfect* and the concept of perfect gas is only theoretical.

(2) Gases tend to show ideal behaviour more and more as the temperature rises above the boiling point of their liquefied forms and the pressure is lowered. Such gases are known as *real or non ideal gases*. Thus, a "*real gas is that which obeys the gas laws under low pressure or high temperature*".

(3) The deviations can be displayed, by plotting the *P-V* isotherms of real gas and ideal gas.



Plot of pressure against volume for ideal and real gases

(4) It is difficult to determine quantitatively the deviation of a real gas from ideal gas behaviour from the *P-V* isotherm curve as shown above. Compressibility factor *Z* defined by the equation,

$$PV = ZnRT \text{ or } Z = PV/nRT = PV_m/RT$$

is more suitable for a quantitative description of the deviation from ideal gas behaviour.

(5) Greater is the departure of Z from unity, more is the deviation from ideal behaviour. Thus, when

(i) $Z = 1$, the gas is ideal at all temperatures and pressures. In case of N_2, the value of Z is close to 1 at $50^{\circ}C$. This temperature at which a real gas exhibits ideal behaviour, for considerable range of pressure, is known as *Boyle's temperature or Boyle's point* (T_B).

(ii) $Z > 1$, the gas is less compressible than expected from ideal behaviour and shows positive deviation, usual at high P *i.e.* $PV > RT$.

(iii) $Z < 1$, the gas is more compressible than expected from ideal behaviour and shows negative deviation, usually at low P *i.e.* $PV < RT$.

(iv) $Z > 1$ for H_2 and He at all pressure *i.e.*, always shows positive deviation.

(v) The most easily liquefiable and highly soluble gases (NH_3, SO_2) show larger deviations from ideal behaviour *i.e.* $Z << 1$.

(vi) Some gases like CO_2 show both negative and positive deviation.

(6) ***Causes of deviations of real gases from ideal behaviour*** **:** The ideal gas laws can be derived from the kinetic theory of gases which is based on the following two important assumptions,

(i) The volume occupied by the molecules is negligible in comparison to the total volume of gas.

(ii) The molecules exert no forces of attraction upon one another. It is because neither of these assumptions can be regarded as applicable to real gases that the latter show departure from the ideal behaviour.

Vander Waal's equation.

(1) To rectify the errors caused by ignoring the intermolecular forces of attraction and the volume occupied by molecules, Vander Waal (in 1873) modified the ideal gas equation by introducing two corrections,

(i) Volume correction

(ii) Pressure correction

(2) Vander Waal's equation is obeyed by the real gases over wide range of temperatures and pressures, hence it is called *equation of state for the real gases.*

(3) The Vander Waal's equation for *n moles* of the gas is,

$$\boxed{\underbrace{\left(P+\frac{n^2a}{V^2}\right)}_{\substack{\text{Pressure correction}\\ \text{for molecular attraction}}} \underbrace{[V-nb]}_{\substack{\text{Volume correction for}\\ \text{finite size of molecules}}} = nRT}$$

a and b are Vander Waal's constants whose values depend on the nature of the gas. Normally for a gas $a >> b$.

(i) **Constant *a*** : It is a indirect measure of magnitude of attractive forces between the molecules. Greater is the value of *a*, more easily the gas can be liquefied. Thus the easily liquefiable gases (like $SO_2 > NH_3 > H_2S > CO_2$) have high values than the permanent gases (like $N_2 > O_2 > H_2 > He$).

Units of '*a*' are : $atm.\, L^2\, mol^{-2}$ or $atm.\, m^6 mol^{-2}$ or $N\, m^4\, mol^{-2}$ (S.I. unit).

(ii) **Constant *b*** : Also called co-volume or excluded volume,

$$\boxed{b = 4N_0 v\left(= \frac{4}{3}\pi r^3\right)}$$

It's value gives an idea about the effective size of gas molecules. Greater is the value of *b*, larger is the size and smaller is the compressible volume. As *b* is the effective volume of the gas molecules, the constant value of *b* for any gas over a wide range of temperature and pressure indicates that the *gas molecules are incompressible*.

Units of '*b*' are : $L\, mol^{-1}$ or $m^3\, mol^{-1}$ (S.I. unit)

(iii) Vander Waal's constant for some gases are,

Name of gas	***a***		***b***	
	atm $litre^2 mol^{-2}$	$Nm^4 mol^{-2}$	**litre** mol^{-1}	$m^3 mol^{-1}$
Hydrogen	**0.245**	**0.0266**	**0.0266**	**0.0266**
Oxygen	**1.360**	**0.1378**	**0.0318**	**0.0318**
Nitrogen	**1.390**	**0.1408**	**0.039**	**0.0391**
Chlorine	**6.493**	**0.6577**	**0.0562**	**0.0562**
Carbon dioxide	**3.590**	**0.3637**	**0.0428**	**0.0428**
Ammonia	**4.170**	**0.4210**	**0.0371**	**0.0371**
Sulphur dioxide	**6.170**	**0.678**	**0.0564**	**0.0564**
Methane	**2.253**		**0.0428**	

(iv) The two Vander Waal's constants and Boyle's temperature (T_B) are related as, $\boxed{T_B = \frac{a}{bR}}$

(4) **Vander Waal's equation at different temperature and pressures :**

(i) **When pressure is extremely low** : For one mole of gas,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ or } PV = RT - \frac{a}{V} + Pb + \frac{ab}{V^2}$$

(ii) **When pressure is extremely high :** For one mole of gas,

$$PV = RT + Pb\,;\ \frac{PV}{RT} = 1 + \frac{Pb}{RT} \quad \text{or} \quad Z = 1 + \frac{Pb}{RT}$$

where *Z* is compressibility factor.

(iii) **When temperature is extremely high :** For one mole of gas,

$PV = RT$.

(iv) **When pressure is low :** For one mole of gas,

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \text{ or } PV=RT+Pb-\frac{a}{V}+\frac{ab}{V^2} \text{ or } \frac{PV}{RT}=1-\frac{a}{VRT} \text{ or } Z=1-\frac{a}{VRT}$$

(v) **For hydrogen :** Molecular mass of hydrogen is small hence value of 'a' will be small owing to smaller intermolecular force. Thus the terms $\frac{a}{V}$ and $\frac{ab}{V^2}$ may be ignored. Then Vander Waal's equation becomes,

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

In case of hydrogen, compressibility factor is always greater than one.

(5) **Merits of Vander Waal's equation :**

(i) The Vander Waal's equation holds good for real gases upto moderately high pressures.

(ii) The equation represents the trend of the isotherms representing the variation of PV with P for various gases.

(iii) From the Vander Waal's equation it is possible to obtain expressions of Boyle's temperature, critical constants and inversion temperature in terms of the Vander Waal's constants 'a' and 'b'.

(iv) Vander Waal's equation is useful in obtaining a 'reduced equation of state' which being a general equation of state has the advantage that a single curve can be obtained for all gases when the equation if graphically represented by plotting the variables.

(6) **Limitations of Vander Waal's equation :**

(i) This equation shows appreciable deviations at too low temperatures or too high pressures.

(ii) The values of Vander Waal's constants a and b do not remain constant over the entire ranges of T and P, hence this equation is valid only over specific range of T and P.

(7) **Other equations of state :** In addition to Vander Waal's equation, there are also equations of state which have been used to explain real behaviour of gases are,

(i) **Clausius equation :** $\left[P+\frac{a}{T(V+c)^2}\right](V-b)=RT$. Here '$c$' is another constant besides a, b and R.

(ii) **Berthelot equation :** $\left(P+\frac{a}{TV^2}\right)(V-b)=RT$.

(iii) **Wohl equation :** $P=\frac{RT}{(V-b)}-\frac{a}{V(V-b)}+\frac{c}{V^2}$

(iv) **Dieterici equation :** $P=\frac{RT}{V-b}.e^{-a/RTV}$. The expression is derived on the basis of the concept that molecules near the wall will have higher potential energy than those in the bulk.

(v) **Kammerlingh Onnes equation :** It is the most general or satisfactory expression as equation expresses PV as a power series of P at a given temperature.

$$PV = A + BP + CP^2 + DP^3 + \ldots\ldots$$

Here coefficients A, B, C etc. are known as first, second and third etc. virial coefficients.

(a) Virial coefficients are different for different gases.

(b) At very low pressure, first virial coefficient, $A = RT$.

(c) At high pressure, other virial coefficients also become important and must be considered.

The critical state.

(1) A state for every substance at which the vapour and liquid states are indistinguishable is known as *critical state*. It is defined by critical temperature and critical pressure.

(2) **Critical temperature (T_c)** of a gas is that temperature above which the gas cannot be liquified however large pressure is applied. It is given by, $\boxed{T_c = \frac{8a}{27Rb}}$

(3) **Critical pressure (P_c)** is the minimum pressure which must be applied to a gas to liquify it at its critical temperature. It is given by, $\boxed{P_c = \frac{a}{27b^2}}$

(4) **Critical volume (V_c)** is the volume occupied by one mole of the substance at its critical temperature and critical pressure. It is given by, $\boxed{V_c = 3b}$

(5) **Critical compressibility factor (Z_c)** is given by, $\boxed{Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375}$

A gas behaves as a Vander Waal's gas if its critical compressibility factor (Z_c) is equal to 0.375.

Note : ✹ A substance in the gaseous state below T_c is called *vapour* and above T_c is called *gas*.

The principle of corresponding states.

(1) In 1881, Vander Waal's demonstrated that if the pressure, volume and temperature of a gas are expressed in terms of its P_c, V_c and T_c, then an important generalization called the principle of corresponding states would be obtained.

(2) According to this principle, "*If two substances are at the same reduced temperature (θ) and pressure (π) they must have the same reduced volume (ϕ),*" i.e. $\boxed{\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta}$

where, $\phi = V/V_c$ or $V = \phi V_c$; $\pi = P/P_c$ or $P = \pi P_c$; $\theta = T/T_c$ or $T = \theta T_c$

This equation is also called ***Vander Waal's reduced equation of state***. This equation is applicable to all substances (liquid or gaseous) irrespective of their nature, because it is not involving neither of the characteristic constants.

(3) This principle has a great significance in the study of the relationship between physical properties and chemical constitution of various liquids.

Degrees of freedom of a gaseous molecule.

(1) The motion of atoms and molecules is generally described in terms of the degree of freedom which they possess.

(2) The *degrees of freedom* of a molecule are defined as the independent number of parameters required to describe the state of the molecule completely.

(3) When a gaseous molecule is heated, the energy supplied to it may bring about three kinds of motion in it, these are,

(i) The translational motion (ii) The rotational motion (iii) The vibrational motion.

This is expressed by saying that the molecule possesses translational, rotational and vibrational degrees of freedom.

(4) For a molecule made up of N atoms, total degrees of freedom = $3N$. Further split up of these is as follows :

		Translational	Rotational	Vibrational
For linear molecule	:	3	2	$3N-5$
For non-linear molecule	:	3	3	$3N-6$

Specific and Molar heat capacity of Gases.

(1) ***Specific heat (or specific heat capacity)*** of a substance is the quantity of heat (in *calories*, *joules*, *kcal*, or *kilo joules*) required to raise the temperature of 1g of that substance through 1^oC. It can be measured at constant pressure (c_p) and at constant volume (c_v).

(2) ***Molar heat capacity*** of a substance is the quantity of heat required to raise the temperature of 1 *mole* of the substance by 1^oC.

$\therefore$ Molar heat capacity = Specific heat capacity × Molecular weight, *i.e.*,

$$C_v = c_v \times M \text{ and } C_p = c_p \times M.$$

(3) Since gases upon heating show considerable tendency towards expansion if heated under constant pressure conditions, an additional energy has to be supplied for raising its temperature by 1^oC relative to that required under constant volume conditions, *i.e.*,

$$C_p > C_v \text{ or } C_p = C_v + \text{Work done on expanson}, P\Delta V(=R)$$

where, C_p = molar heat capacity at constant pressure; C_v = molar heat capacity at constant volume.

Note : ✹ C_p and C_v for solids and liquids are practically equal. However, they differ considerable in case of gas because appreciable change in volume takes place with temperature.

(4) **Some useful relations of C_p and C_v**

(i) $C_p - C_v = R = 2\,calories = 8.314J$

(ii) $C_v = \frac{3}{2}R$ (for monoatomic gas) and $C_v = \frac{3}{2} + x$ (for *di* and polyatomic gas), where x varies from gas to gas.

(iii) $\frac{C_p}{C_v} = \gamma$ (Ratio of molar capacities)

(iv) For monoatomic gas $C_v = 3\,calories$ whereas, $C_p = C_v + R = 5calories$

(v) For monoatomic gas, $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$.

(vi) For diatomic gas $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

(vii) For triatomic gas $(\gamma) = \frac{C_p}{C_v} = \frac{8R}{6R} = 1.33$

Values of Molar heat capacities of some gases,

Gas	C_p	C_v	$C_p - C_v$	$C_p/C_v = \gamma$	Atomicity
He	5	3.01	1.99	1.661	1
N_2	6.95	4.96	1.99	1.4	2
O_2	6.82	4.83	1.99	1.4	2
CO_2	8.75	6.71	2.04	1.30	3
H_2S	8.62	6.53	2.09	1.32	3

Liquefaction of gases.

(1) A gas may be liquefied by cooling or by the application of high pressure or by the combined effect of both. The first successful attempt for liquefying gases was made by ***Faraday (1823)***.

(2) Gases for which the intermolecular forces of attraction are small such as H_2, N_2, Ar and O_2, have low values of T_c and cannot be liquefied by the application of pressure are known as "permanent gases" while the gases for which the intermolecular forces of attraction are large, such as polar molecules NH_3, SO_2 and H_2O have high values of T_c and can be liquefied easily.

(3) **Methods of liquefaction of gases :** The modern methods of cooling the gas to or below their T_c and hence of liquefaction of gases are done by Linde's method and Claude's method.

(i) **Linde's method :** This process is based upon ***Joule-Thomson effect*** which states that "When a gas is allowed to expend adiabatically from a region of high pressure to a region of extremely low pressure, it is accompained by cooling."

(ii) **Claude's method :** This process is based upon the principle that when a gas expands adiabatically against an external pressure (as a piston in an engine), it does some external work. Since work is done by the molecules at the cost of their kinetic energy, the temperature of the gas falls causing cooling.

(iii) By adiabatic demagnetisation.

(4) **Uses of liquefied gases :** Liquefied and gases compressed under a high pressure are of great importance in industries.

(i) Liquid ammonia and liquid sulphur dioxide are used as refrigerants.

(ii) Liquid carbon dioxide finds use in soda fountains.

(iii) Liquid chlorine is used for bleaching and disinfectant purposes.

(iv) Liquid air is an important source of oxygen in rockets and jet-propelled planes and bombs.

(v) Compressed oxygen is used for welding purposes.

(vi) Compressed helium is used in airships.

(5) **Joule-Thomson effect :** When a real gas is allowed to expand adiabatically through a porous plug or a fine hole into a region of low pressure, it is accompanied by cooling (except for hydrogen and helium which get warmed up).

Cooling takes place because some work is done to overcome the intermolecular forces of attraction. As a result, the internal energy decreases and so does the temperature.

Ideal gases do not show any cooling or heating because there are no intermolecular forces of attraction i.e., they do not show Joule-Thomson effect.

During Joule-Thomson effect, enthalpy of the system remains constant.

Joule-Thomson coefficient. $\mu = (\partial T/\partial P)_H$. For cooling, $\mu = +ve$ (because dT and dP will be $-ve$) for heating $\mu = -ve$ (because $dT = +ve, dP = -ve$). For no heating or cooling $\mu = 0$ (because $dT = 0$).

(6) **Inversion temperature :** It is the temperature at which gas shows neither cooling effect nor heating effect *i.e.*, Joule-Thomson coefficient $\mu = 0$. Below this temperature, it shows cooling effect and above this temperature, it shows heating effect.

Any gas like H_2, He etc, whose inversion temperature is low would show heating effect at room temperature. However, if these gases are just cooled below inversion temperature and then subjected to Joule-Thomson effect, they will also undergo cooling.